Environment CANADA Environnement
1020926I VOL ISS 64 850700
EXC # 001
TD 171.5.C3 R46
REPORT EE

OOFF

A MODEL OF THE LONG-TERM FATE OF CHEMICAL SPILLS

FF-64

A MODEL OF THE LONG-TERM FATE OF CHEMICAL SPILLS

by

D. Mackay
S. Paterson
University of Toronto
Toronto, Ontario

This report has not undergone detailed technical review by the Environmental Protection Service and the content does not necessarily reflect the views and policies of Environment Canada. Mention of trade names or commercial products does not constitute endorsement for use.

This unedited version is undergoing a limited distribution to transfer the information to people working in related studies. This distribution is not intended to signify publication and, if the report is referenced, the author should cite it as an unpublished report of the Branch indicated below.

Any comments concerning its content should be directed to:

Environmental Emergencies Technology Division
Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Environment Canada
Ottawa, Ontario
K1A 1C8

EE-64

July, 1985

ABSTRACT

A computer model has been developed and tested which describes the long term behaviour of a chemical spill or the residues from a spill. It treats five compartments (air, water, soil, groundwater and bottom sediment) and has the facility to include fish and suspended sediment compartments. The physical-chemical and reaction properties of the chemical are entered into the program. A specified amount of chemical is introduced into one or more compartments and the rates of transfer to other compartments, of reaction and (if desired) of advection, are calculated. The amounts and concentrations of chemical in each compartment are computed as a function of time until the chemical is essentially removed.

The model has been tested on eight chemicals which are either frequently spilled or for which satisfactory data exist, namely linear alkylbenzenesulphonate, trichloroethylene, Arocior 1242, Aldicarb, p-cresol, dieldrin, ethylene dichloride and acetone. The computed and generally observed performances are in satisfactory agreement. Improvements could be made in the output but this requires guidance from emergency response personnel. The model involves numerical integration of a set of five simultaneous differential equation using a novel, robust method which requires little memory. The calculation can be readily done on a portable micro-computer.

CONTENTS

Abstract	i
Contents	ii
1. Introduction	1
2. Model Structure	2
3. Illustration	10
4. Results	15
5. Discussion	38
6. Conclusion	40
7. References	41

Appendix

Computer Program

1. INTRODUCTION.

When a chemical is accidentally spilled its behaviour in the short term of hours and days is normally quantified by calculating the rates of processes such as spreading, permeation into soil, dissolution or emulsification into water, evaporation and subsequent atmospheric dispersion. Normally an attempt is made to contain and recover the spilled material but in some cases this may not be feasible because of technical, economic, fire hazard or toxicity considerations. The spill may be in a remote location in which countermeasures are delayed. Usually, some residue of the spill remains unrecovered. Decisions must then be made about the desirability of further clean-up. In some instances the best policy may be to leave the spilled material alone to degrade and disperse naturally.

When making such decisions it is useful to have available an assessment of the long term (i.e. months and years) behavior of the chemical. For example, if it is a very persistent substance which will bioconcentrate in fish, further cleanup may be desirable. A potential groundwater contaminant should not be allowed to continue to permeate into soil. On the other hand, a chemical which hydrolyses rapidly in water may pose little hazard if allowed to flow into a creek. Usually the chemical data available to the emergency response team does not include such information, although they may have certain indicators of likely behaviour in the form of properties such as vapour pressures or octanol-water partition coefficients. There is thus a need for a computer program or model which can accept such data then calculate the likely fate of the chemical and present the findings rapidly and clearly.

The purpose of this work is to devise and illustrate such a model, and explore further possibilities. The model is a novel version of the Level IV Fugacity evaluative environmental model as described by Mackay and Paterson (1982). A number of changes in model structure have been made to improve its performance in emergency response situations. The significant changes are as follows:

- The number of compartments has been reduced, but a groundwater compartment has been added. The compartments treated are air, soil, water column, groundwater and bottom sediment.

o Although fish and suspended solids are not treated as separate compartments, concentrations in these phases are calculated.

o The environment size can be varied as desired.

o Overall reaction rates are inserted in the form of estimated half-lives for each compartment.

o The method of solving the equations has been simplified to make the system more robust and solution more rapid.

o Only essential data are printed out.

o The computer memory requirements have been minimized in order that a portable computer can be used.

It is emphasised that this model is not regarded as the ultimate version. Improvements can undoubtedly be made, especially in the light of operating experience.

In this report Chapter 2 describes the model, a complete listing being given in the Appendix. Chapter 3 is an illustration of the output for selected chemicals. Chapter 4 is a discussion of the results and finally Chapter 5 presents conclusions and recommendations.

2. MODEL STRUCTURE.

The fugacity concept as applied to environmental calculations has been described by Mackay and Paterson (1982) and no effort is made here to justify the assumptions or fully describe all the variables. The Level IV version used here exploits the inter-phase transport expressions derived in a recent Level III model described by Mackay et al. (1985). It should be noted that the model is primarily designed for use with organic chemicals. Usually the behaviour of inorganic chemicals is easier to predict.

Figure 2.1 shows the compartments, the reaction processes and the transport mechanisms. The volumes, areas and properties of each compartment are listed.

Table 2.1 gives the chemical properties which are used in the calculations and expressions for calculating fugacity capacities.

Table 2.2 gives the expressions used for calculating inter-compartment transfer rates and reaction and advection rates. Reactions are assumed to be first order.

A total amount (kg) of chemical spilled is entered and a specification made of its initial percentage disposition into the five compartments. The chemical is assumed to be homogeneously distributed throughout the volume reflecting a situation which may be reached some days after spillage. There is no provision for a separate chemical phase since this greatly increases the complexity of the system. This could be a desirable feature of future models.

The calculation is essentially the solution of five simultaneous first order differential equations which when applied to compartment i express the amount of chemical M_i mols as

$$d(M_i)/dt = d(V_i Z_i F_i)/dt = \sum F_j D_{ji} - F_i \sum D_{ij} \qquad (2.1)$$

where the D terms are transport and transformation parameters, V_i is volume, Z_i is fugacity capacity and F_i is fugacity. The conventional method of solving such equations is a finite difference approach or a variation of the Runge-Kutta type. Here we adopt a method which is very robust and involves calculating the change in amount dM_i in each compartment separately using the equation

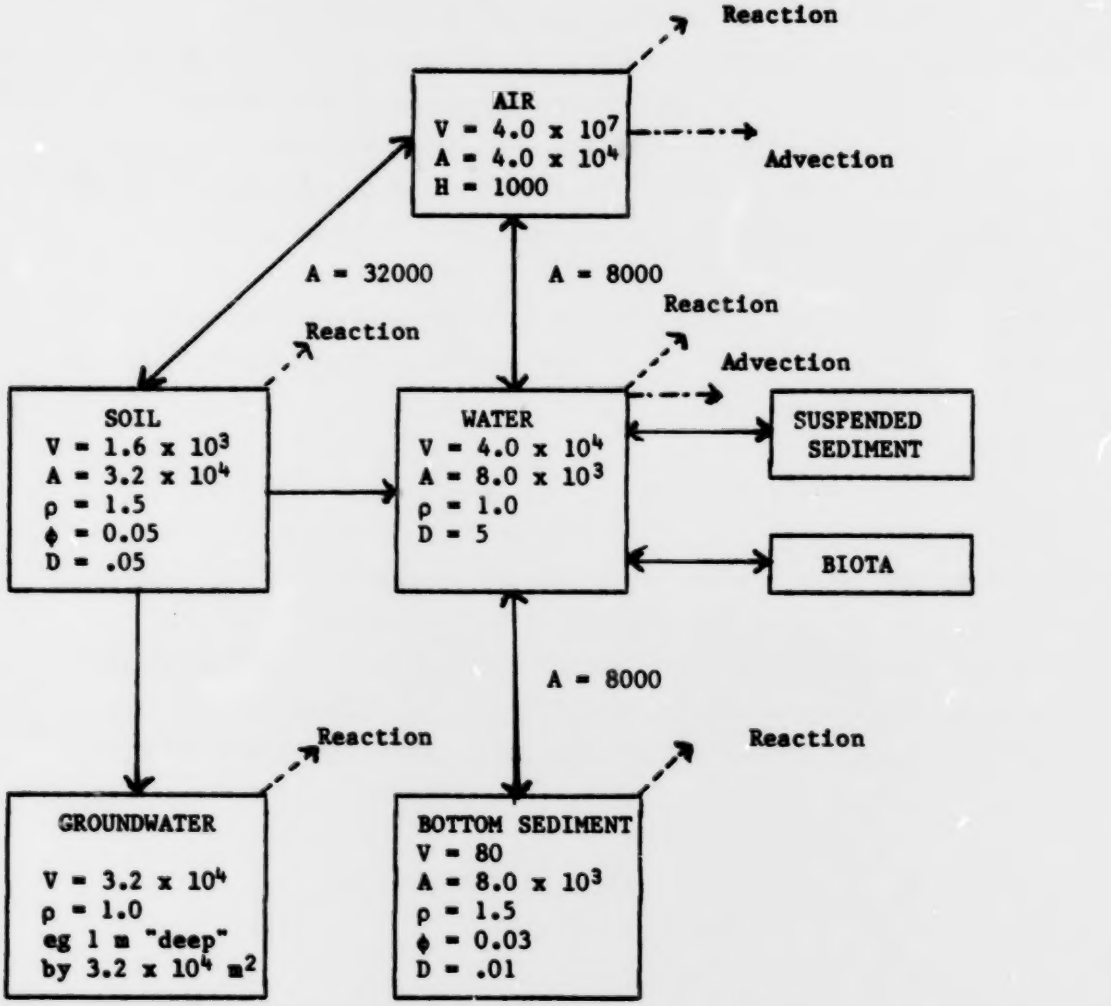
$$dM_i = T_i(\Sigma F_j D_{ji} - F_i \Sigma D_{ij})\ (1-\exp(-dt/T_i))$$
$$\text{where } T_i = V_i Z_i / \Sigma D_{ij} \qquad (2.2)$$

The group T_i is a time constant for transfer from the compartment. The time increment for integration is dt. If dt is much smaller than T_i this reduces to a version of equation 2.1

$$dM_i = dt(\Sigma F_j D_{ji} - F_i \Sigma D_{ij}) \qquad (2.3)$$

The advantage of using this approach is that it is impossible to transfer a quantity of material from a compartment which exceeds the amount in

Figure 2.1 Illustration of transfer and reaction processes and compartment characteristics for an assumed area 200 m square which is 20% water 5 m deep



LEGEND

Interphase Transfer

Reaction

Advection

V - volume (m^3)
A - interfacial area (m^2)
ρ - density (g/cm^3)
φ - fraction organic content
H - height (m)
D - depth (m)

Table 2.1 Definition of Z values

Molecular weight			WM	g/mol
Vapor pressure			VP	Pa
Aqueous solubility			SG	g/m^3
Octanol-water partition coeff.			K_{OW}	
Bioconcentration factor (correlation $K_B = 0.048\ K_{OW}$)			K_B	
Organic carbon partition coeff. (correlation $K_{OC} = 0.411\ K_{OW}$)			K_{OC}	
Z_A	Air		1/RT	$mol/m^3.Pa$
Z_W	Water		SG/(VP.WM)	"
Z_G	Groundwater		SG/(VP.WM)	"
Z_S	Soil ϕ = fraction organic content = 0.05 ρ = density = 1.5 g/cm^3		$Z_W K_{OC} \phi_S \rho_S$	"
Z_B	Bottom sediment ϕ = fraction organic content = 0.03 ρ = density = 1.5 g/cm^3		$Z_W K_{OC} \phi_B \rho_B$	"
Z_S	Suspended sediment ϕ = fraction organic content = 0.03 ρ = density = 1.5 g/cm^3		$Z_W K_{OC} \phi_{SS} \rho_{SS}$	"
Z_F	Biota (fish) ρ = density = 1.0 g/cm^3		$Z_W K_B \rho_F$	"

T = temperature (K) R = 8.314J/molK

Table 2.2. Definition of Coefficients for Interphase Transfer Reaction and Advection

Process	Rate Expression (D Value)	Definition
air ⟶ water	$A_W/(1/K_AZ_A + 1/K_WZ_W)$	K_A = air side MTC = 10 m/h
		K_W = water side MTC = 0.1 m/h
		A_W = interfacial area
air ⟶ soil	$K_SA_SZ_A$	K_S = soil MTC = 0.1 m/h
		A_S = interfacial area
sediment ⟶ water	$K_B'A_WZ_W$	K_B' = sediment MTC = 0.01 m/h
		A_W = interfacial area
water ⟶ sediment	$K_B'A_WZ_W + G_DZ_B$	G_D = sediment deposition rate ≅ 1 mm/yr
soil ⟶ water	G_SZ_W	G_S = soil run-off rate ≅ 0.5 m/yr
soil ⟶ groundwater	G_SZ_W	as above ie equal run-off and groundwater charge

Reaction rates

Compartment	Rate Expression	Definition
air	$0.69\ V_AZ_A/HLA$	HLA = reaction half-life in air
water	$0.69\ V_WZ_W/HLW$	HLW = reaction half-life in water
soil	$0.69\ V_SZ_S/HLS$	HLS = reaction half-life in soil
sediment	$0.69V_BZ_B/HLB$	
groundwater	$0.69\ V_GZ_W/HLG$	

Advection rates

Compartment	Rate Expression	Definition
air	$0.69VAZ_A/HLAA$	HLAA = advective half-life in air = 70 hours
water	$0.69VWZ_W/HLWA$	HLWA = advective half-life in water = 700 hours

In all cases the rate of the processes are products of these D values and the source phase fugacity.

the phase. If, by accident, dt greatly exceeds T_i the exponential group approaches zero and dM_i approaches a maximum of

$$dM_i = T_i(\Sigma F_j D_{ji} - F_i \Sigma D_{ij})$$
$$= V_i Z_i (\Sigma F_j D_{ji} / \Sigma D_{ij}) - V_i Z_i F_i$$

Thus even if there is no transfer in (expressed by the first term), the maximum which can be transferred out is the second term which is the amount in the compartment. This constraint would not apply to a finite difference version of equation. 2.1. i.e. equation 2.3.

The amounts transferred and transformed from each compartment are thus calculated. A potential problem arises in that the amounts exchanged between two compartments e.g. air and water may not be equal as viewed from each compartment due to the different exponential terms. For example, the amount calculated in the water differential equation as being received from the air may exceed the amount in the air and available for transfer. There are various methods of solving this problem but the simplest was adopted, namely to select the smaller of the two transfer amounts. For conservation of mass only one amount must be selected and used.

A final calculation is done of every transport and transformation process rate and the new amounts present in each compartment are calculated, followed by the concentrations, fugacities and percentages. The total amount reacted is calculated and the condition of the chemical printed out essentially as a mass balance. The calculation then returns to the start and repeats the process to any desired time. The concentrations in fish and suspended sediment are calculated and printed out assuming that equilibrium has been reached with the water. In fact there may be a delay in biouptake, but this is not included.

An issue which is frequently the source of some discussion and controversy in evaluative models is the proper role of advection or flow from the region, usually in air and water. Advection may be included as a pseudo reaction by assigning an appropriate half-life and "adding" it to the reaction half-life. The correct addition is of rate constants or reciprocal half-lives, namely if T is half-life

$$1/T_0 = 1/T_1 + 1/T_2 \text{ etc.}$$

where T_1, T_2 etc. are individual half-lives. The overall half-life T_0 is thus less than the smallest individual half-life. This is equivalent to the ohmic resistances-in-parallel problem where T is equivalent to resistance.

Inserting a very short advective half-life (ie having rapid outflow) may distort the output because the chemical may be deduced to "disappear" rapidly. In fact it merely moves out of the area of interest and contaminates another area. It may be appropriate to test several advective half-lives, but if the aim is to predict overall environmental persistence, no advection should be included. Advective half-lives of 70 hours for air and 700 hours for water are used in this model. These half-lives correspond to residence times due to advection of 100 and 1000 hours respectively in these two compartments. They can be varied as desired.

An interesting calculation which can be made quite rapidly is the equilibrium distribution of the chemical in the environment assuming no reaction or advection and rapid inter-compartment transfer. This is a "Level I" calculation and involves calculating V_iZ_i for each compartment and their sum. The fraction in each compartment is then $V_iZ_i/(\Sigma V_iZ_i)$.

The Level II type calculation including reaction but not including transfer resistance can give an approximate overall persistence or time for decay deduced as the amount in the system $\sum(V_iZ_iF_i)$ divided by the rate of reaction or removal $\sum(V_iZ_ik_iF_i)$. Since the F_i values are common this persistence time or reciprocal rate constant is

$$\Sigma V_iZ_i/\Sigma V_iZ_ik_i$$

The half-life is 0.693 times the above value.

The time increment dt is best selected as a convenient number of hours (e.g. 24). It should preferably be smaller than the smallest compartment time constant T_i. The use of larger values introduces some error but speeds the calculation. The selection of dt is made early in the program.

A print-out of the various input parameters is also provided before the calculation starts.

To avoid excessive printing a facility is included to print out only once in a specified number of integration steps.

It should be noted that although the calculations involve the use of fugacities, it is not necessary to understand fugacity or use it, when performing the calculations. Only "conventional" data are requested as are found in, for example, TIPS manuals (Environment Canada 1984) or other Handbooks.

3. IL'.USTRATION.

The model was tested on a number of chemicals which were selected on the following bases: -

1. They are likely candidates for accidental spillage.
2. Adequate physical chemical and reactivity data are available.
3. Some experience exists about their environmental behaviour either generally or in a spill situation.

The chemicals are listed in Table 3.1 with their estimated properties. A brief description of each follows.

Trichloroethylene is a volatile liquid, widely used as a solvent. It is expected to partition primarily into the air.

Aroclor 1242 is a polychlorinated biphenyl mixture which is a long term or persistent contaminant which tends to partition into sediments and bioconcentrate in fish. It is denser than water.

Aldicarb is a pesticide applied to soils which has caused groundwater problems in the U.S.

P-cresol is a phenolic substance which tends to dissolve in water and degrade there.

Dieldrin is a pesticide which has been applied to soils, but which has been subject to runoff and has been found in sediments and in fish (Schnoor et al 1981).

Ethylene dichloride is a volatile solvent which was spilled in a river in B.C. and for which some monitoring data exist (Neely 1985). It is expected to volatilize appreciably from water.

Linear alkylbenzene sulphonate (LAS) is a surfactant which is widely used in detergent formulations. Some data exist on its behavior in rivers (Games 1982).

Acetone is a volatile, water miscible solvent whose environmental fate has been assessed for rivers by Rathbun et al. (1982).

These substances thus cover the range of properties which are likely to be encountered in chemical spills. If the model can predict or reproduce their generally accepted behaviour, it lends some confidence to the use of the model in a predictive mode for other chemicals.

It should be noted that the reactivities or half-lives are in doubt in many cases and there is probably considerable site-to-site and time-to-time variation, especially with seasons of the year.

For a chemical which is totally persistent the true rate constant is zero and the half-life is infinite. The program cannot accept such values, thus a very long half-life of 1 million hours (i.e. 1E06 hours) or over 100 years is inserted. No significant reaction thus takes place in the time frame of the calculation.

Presenting the data from the calculations is best done graphically or pictorially. After some trial and error a plot of log amount or percent (total and in each compartment) against time was selected. The time scale adopted depends on the time of interest to the emergency response group and on the chemical's persistence. A concentration plot may also be useful.

In these illustrative cases, the size of the evaluative environment is 200 m square containing 80% soil, 20% water. The amount spilled, or remaining after clean up, was 100 kg with a disposition as shown in Table 3.2.

It should be noted that these dispositions are regarded as applying some days after the spill takes place. In the case of the PCB, its high density may cause it to move directly to the sediment. It is possible that the amount present in a compartment exceeds the solubility in that compartment. A simple test of this is to compare the fugacity in each compartment with the vapour pressure. Saturation occurs when fugacity equals vapour pressure and a separate phase exists at higher fugacities. Inspection

of the output reveals such situations. Although it is erroneous to have such higher-than-saturation fugacities the effect is to drive the chemical into neighbouring compartments and usually a lower-than-saturation value is reached quite rapidly. The model thus gives a reasonable prediction of behavior under these conditions.

Table 3.1

Properties of the Chemicals

Chemical	Molecular Weight (g/mol)	Vapour Pressure (Pa)	Solubility (g/m^3)	log K_{OW}	Half-Life (h)				
					Air	Water	Soil	Sediment	Groundwater
LAS	348	(.01)*	62.5	4.3**	1E+06	33	17	17	33
TCE	131.4	9.87E+03	1.1E+03	2.29	96	7.7E03	1E+06	1E+06	7.7E+03
Aroclor 1242	261	0.1	0.4	5.0	1E+06	4.6E+04	1.4E+04	1.4E+04	4.6E+04
Aldicarb	190.3	1.33E-02	6.0E+03	0.70	1E+06	5.8E+04	3.69E+02	1E+06	5.8E+04
p-cresol	108.1	1.44E+01	1.8E+03	2.20	1E-06	12.9	1.34	1.34	12.9
Dieldrin	381	2.4E-05	0.1	4.5	1E+03	1E+03	1E+03	1E+03	1E+03
Ethylene dichloride	98.96	7.0E+03	8.5E+03	1.48	2.4E+03	1E+06	1E+06	1E+06	1E+06
Acetone	58.08	1.6E+04	2.6E-05	-0.24	1E+06	0.16	1E+06	1E+06	0.16

* this value is fictitious, but does not affect the result.
** this value is believed to be too large but gives the correct sorption partition coefficient.

Table 3.2

Initial Percentage Distribution of Spilled Compounds

Compound	Percentage Distribution				
	air	soil	water	Bottom sediment	groundwater
Ethylene dichloride	0	0	100	0	0
p-Cresol	0	50	50	0	0
Aroclor 1242	0	80	10	10	0
Aldicarb	0	100	0	0	0
Trichloroethylene	10	80	10	0	0
Dieldrin	10	80	10	0	0
LAS	0	0	100	0	0
Acetone	0	50	50	0	0

4. RESULTS.

Figures 4.1 to 4.4 illustrate the behavior of ethylene dichloride with and without advection expressed as concentration and amount. The available observations (Neely 1985) suggest a relatively short half-life when spilled in a river with considerable evaporation. Comparing Figures 4.1 and 4.2 (amounts with and without advection) suggests that it is desirable to include advection since the total amount decreased by a factor of 10 in a reasonable 12 days with advection but in an unreasonably long 350 days without advection. It was thus decided to include advection in all subsequent assessments.

The general behaviour of the chemical (here spilled 100% into water) is to evaporate rapidly, most of the amount being in the air but at low concentrations. The water concentration falls from approximately 1 g/m^3 to 0.1 g/m^3 in 9 days (Figure 4.3) then to 0.01 g/m^3 in 17 days followed by a factor of 10 drop each 8 days thereafter. Some transfer is predicted to occur from water to air to soil to groundwater but the amount is slight ie 0.01%. Essentially, any amounts falling two or more log scales below the initial amount can be ignored. Only water and air are important.

For interest Figure 4.5, is a plot of fugacity versus time is included showing the expected high values in water with air values approximately a factor of two lower.

P-cresol (Figures 4.6 and 4.7) was spilled 50% each in soil and water. There is a rapid drop in soil amount due to degradation and runoff. The water concentration falls by a factor of 10 in 48 hours thus this chemical is short lived. Little enters sediment, groundwater or air and although not shown, little bioconcentrates. The highest concentrations are found in water.

Aroclor 1242 (Figures 4.8 and 4.9) was spilled in soil, water and sediment, the latter being due to sinking. Most remains in the soil with a long persistence corresponding to a factor of 10 drop in about 4 years. About 0.1% enters groundwater. This is a small amount but the concentration is of concern since it approaches 0.00004 mol/m^3 or approximately 0.01 g/m^3 ie 10

parts per billion. Relatively high sediment and fish concentrations would be expected.

Aldicarb (Figures 4.0 and 4.11) is spilled 100% into soil and partitions rapidly into the groundwater due to its low octanol-water partition coefficient. A negligible amount evaporates. It remains in the groundwater with almost constant concentration for many years. This is consistent with observed persistence in groundwater.

Trichloroethylene (Figures 4.12 and 4.13) was spilled 80% in soil and 10% each in air and water. It is removed rapidly from soil and less rapidly from air and water at a rate of a factor of 10 in 5 days. Fairly high concentrations are found in sediment and groundwater which are shielded from evaporation.

Dieldrin (Figures 4.14 and 4.15) was spilled 80% in soil and 10% each in air and water. It tends to remain associated with soil with about 1/20th the amount in sediment. It takes about 200 days to fall a factor of ten in amount. The highest concentrations are found in soil and sediment. High concentrations would also be expected in fish.

LAS spilled into water tends to remain in water, falling in amount by a factor of 10 in 5 days. The highest concentrations are encountered in sediment. It is thus not a particularly persistent chemical. It does not evaporate.

Acetone (figures 4.18 and 4.19) is distributed 50% each into soil and water. Vaporization and biodegradation reduce the water concentration by a factor of 10 in 18 hours. Soil loss is also rapid due to evaporation. After 24 hours, most of the compound is in the air where it will be slowly removed by advection. These results agree with Rathburn et al 1982 who concluded that

volatilization and biodegradation were the processes most likely to dominate the fate of acetone spilled in water.

Figure 4.20 is a specimen output in text form for ethylene dichloride. At selected intervals a mass balance can be printed out as illustrated in that diagram. Concentrations in fish and suspended sediment are given, but these were not printed out in the graphs to avoid excessively crawded data. The concentrations in these phases are generally similar to those in the sediment.

Figure 4.1

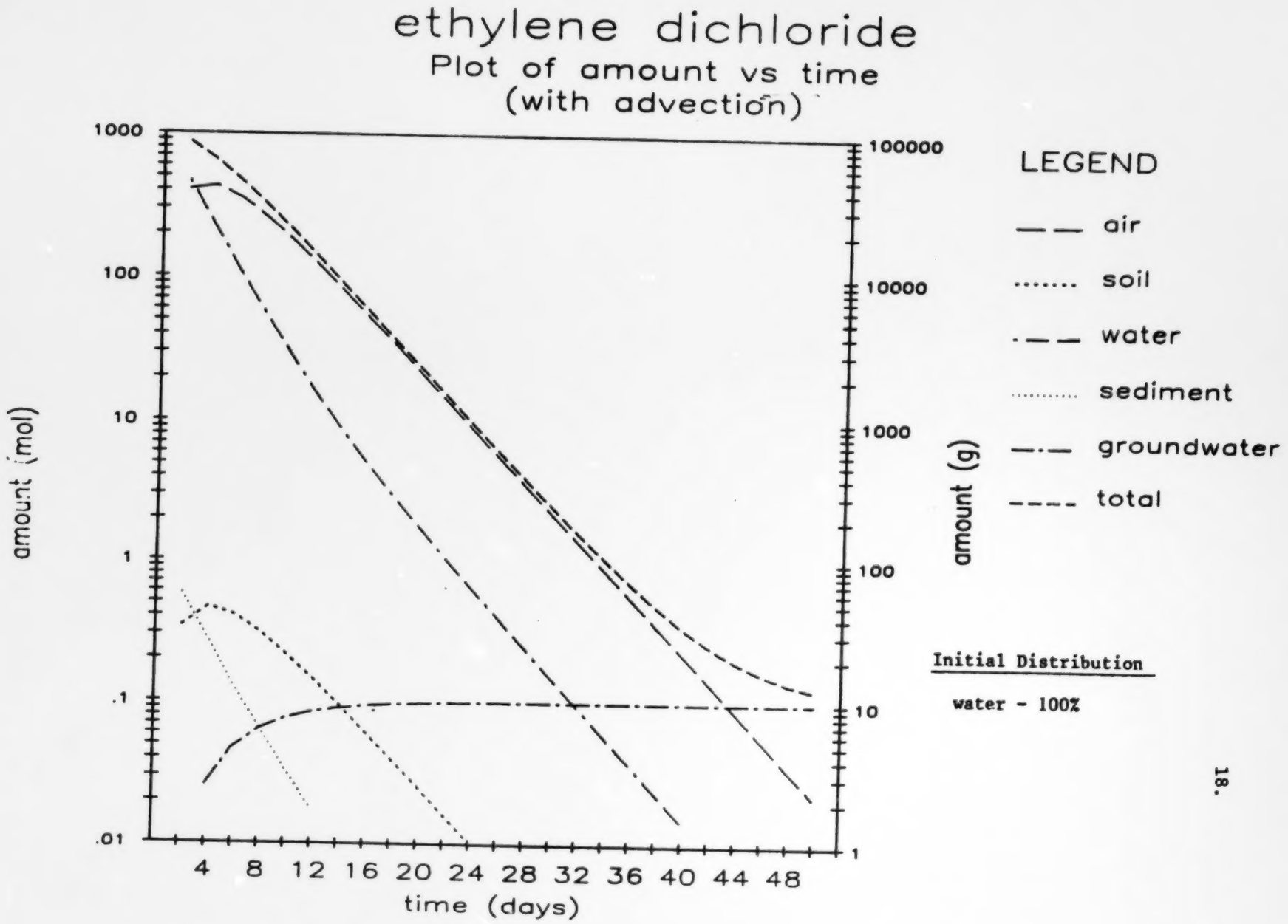

ethylene dichloride
Plot of amount vs time
(with advection)
amount (mol)
1000
100
10
1
.1
.01
amount (g)
100000
10000
1000
100
10
1
4 8 12 16 20 24 28 32 36 40 44 48
time (days)
LEGEND
air
soil
water
sediment
groundwater
total
Initial Distribution
water - 100%

Figure 4.2

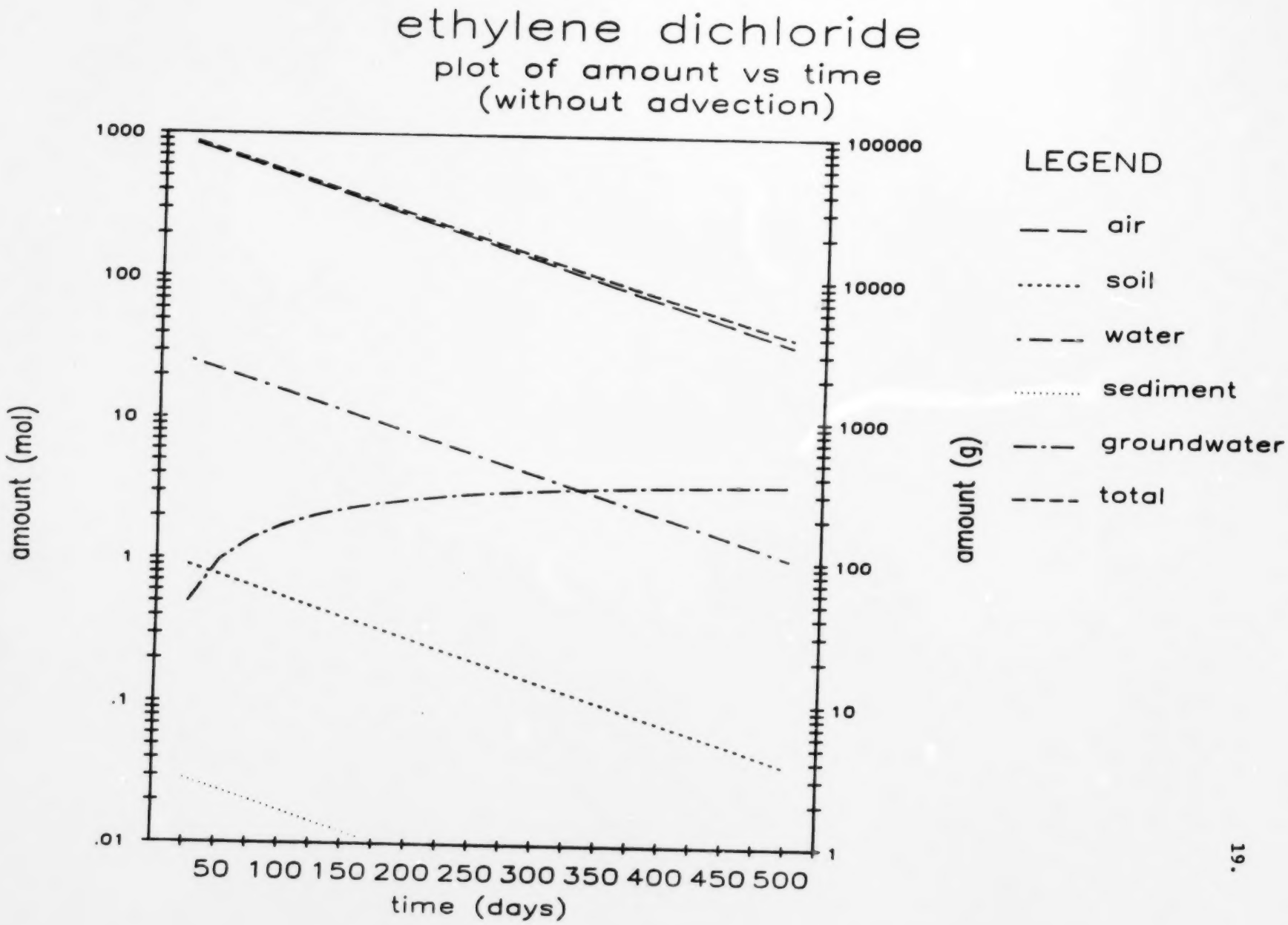

ethylene dichloride
plot of amount vs time
(without advection)
amount (mol)
1000
100
10
1
.1
.01
amount (g)
100000
10000
1000
100
10
1
50 100 150 200 250 300 350 400 450 500
time (days)
LEGEND
air
soil
water
sediment
groundwater
total

Figure 4.3

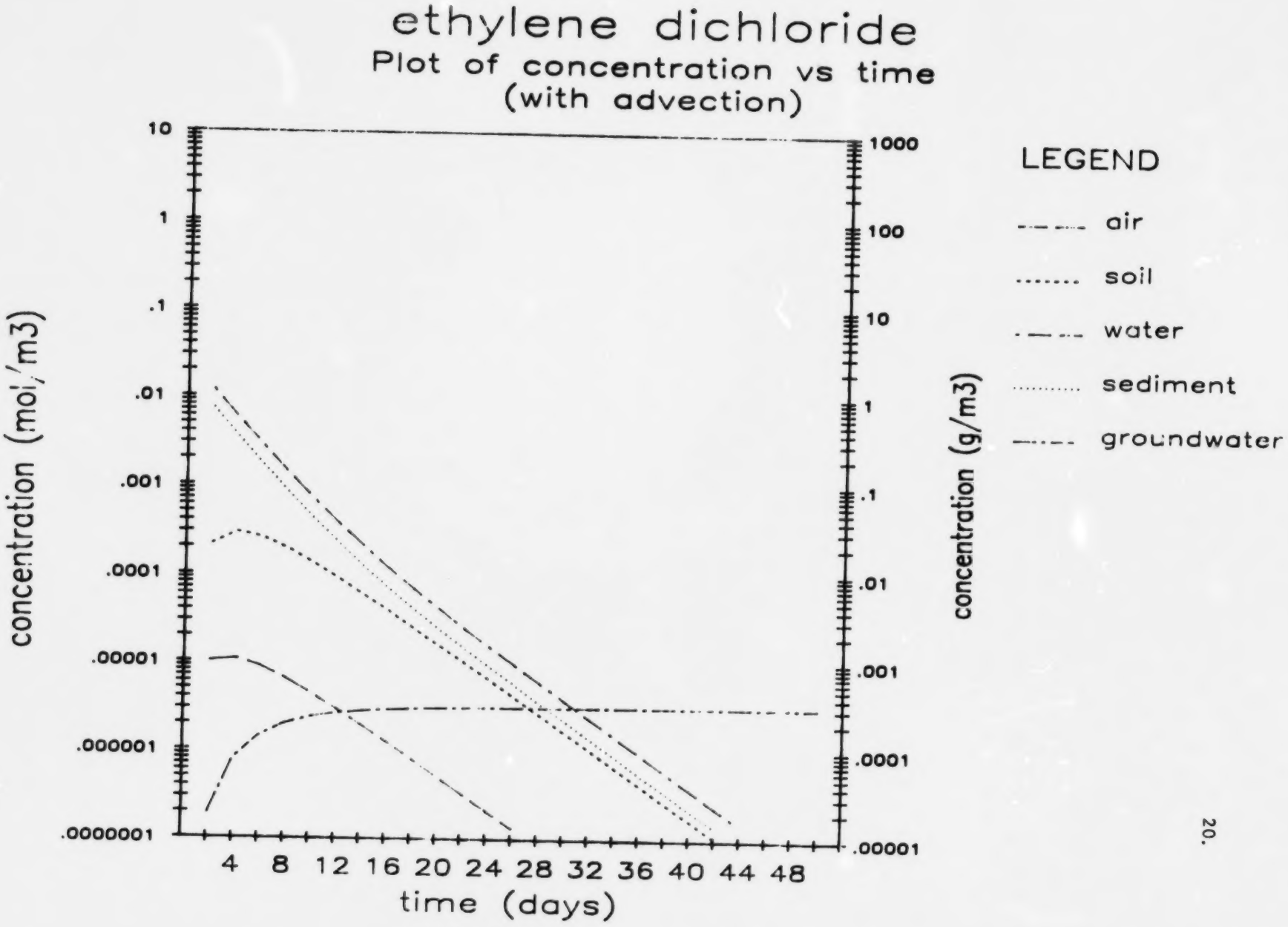

ethylene dichloride
Plot of concentration vs time
(with advection)
concentration (mol/m3)
10
1
.1
.01
.001
.0001
.00001
.000001
.0000001
concentration (g/m3)
1000
100
10
1
.1
.01
.001
.0001
.00001
4 8 12 16 20 24 28 32 36 40 44 48
time (days)
LEGEND
air
soil
water
sediment
groundwater

Figure 4.4

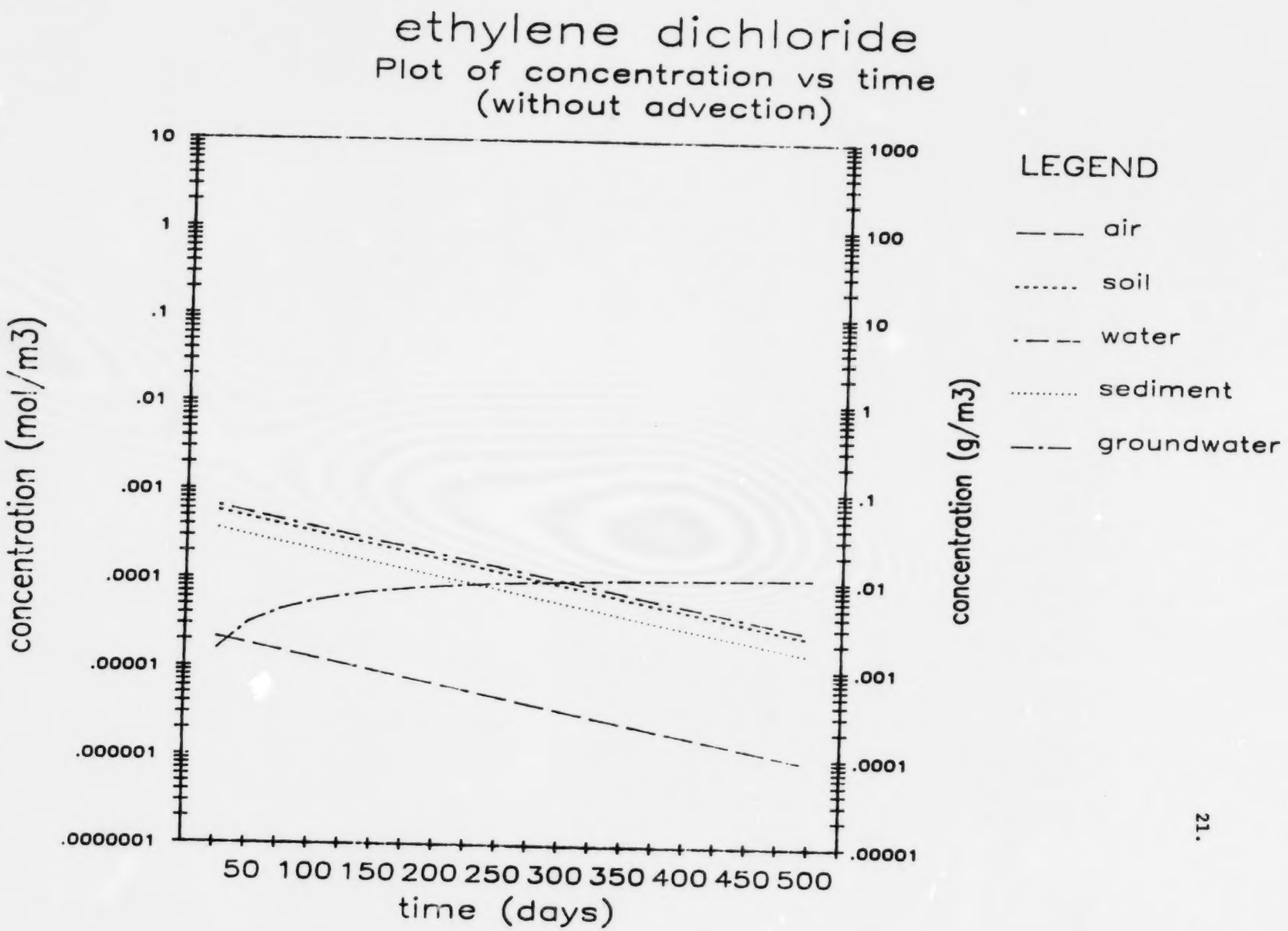

ethylene dichloride
Plot of concentration vs time
(without advection)
concentration (mol/m3)
10
1
.1
.01
.001
.0001
.00001
.000001
.0000001
concentration (g/m3)
1000
100
10
1
.1
.01
.001
.0001
.00001
50 100 150 200 250 300 350 400 450 500
time (days)
LEGEND
air
soil
water
sediment
groundwater

Figure 4.5

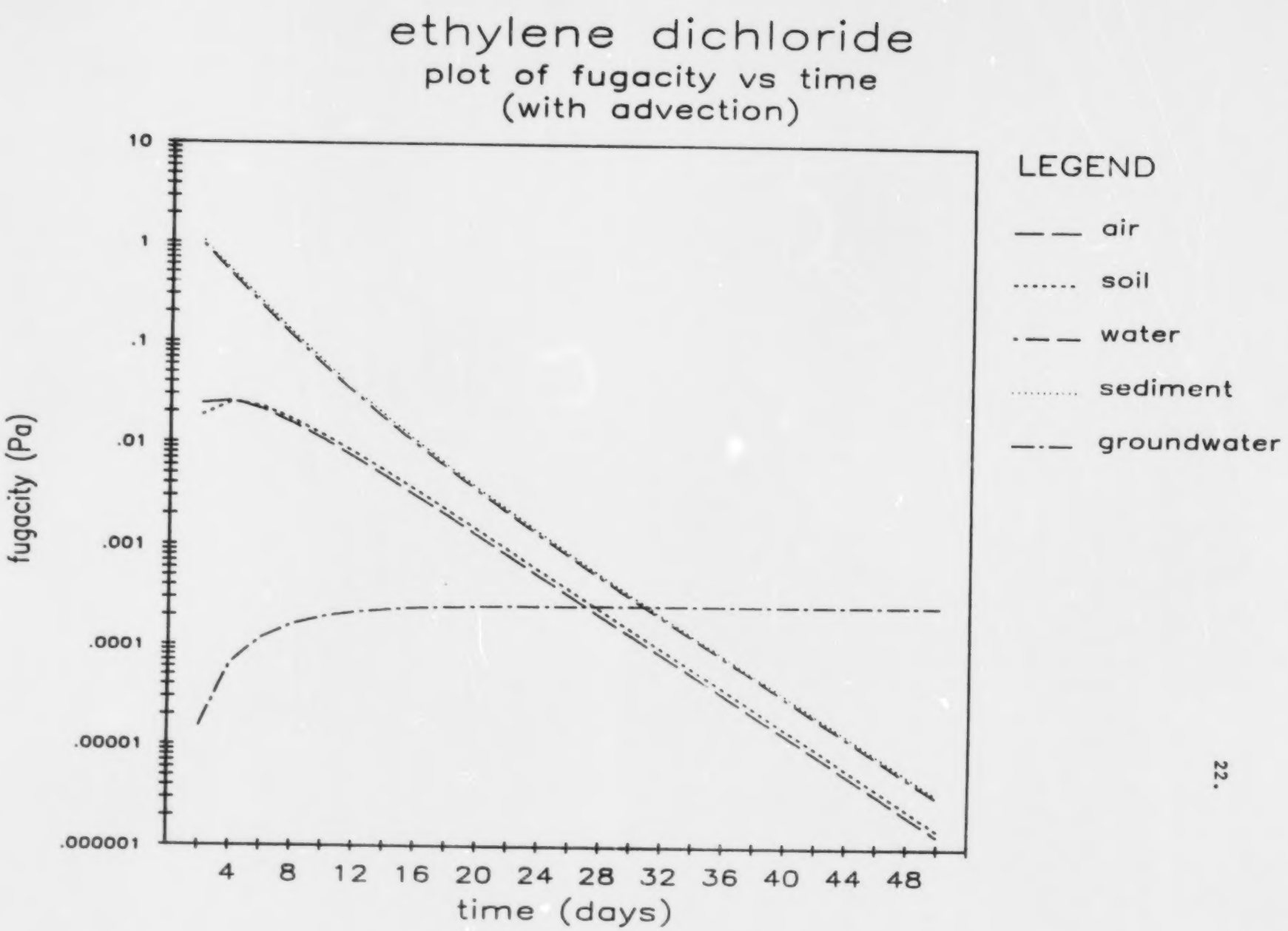

ethylene dichloride
plot of fugacity vs time
(with advection)
fugacity (Pa)
10
1
.1
.01
.001
.0001
.00001
.000001
4
8
12
16
20
24
28
32
36
40
44
48
time (days)
LEGEND
air
soil
water
sediment
groundwater

Figure 4.6

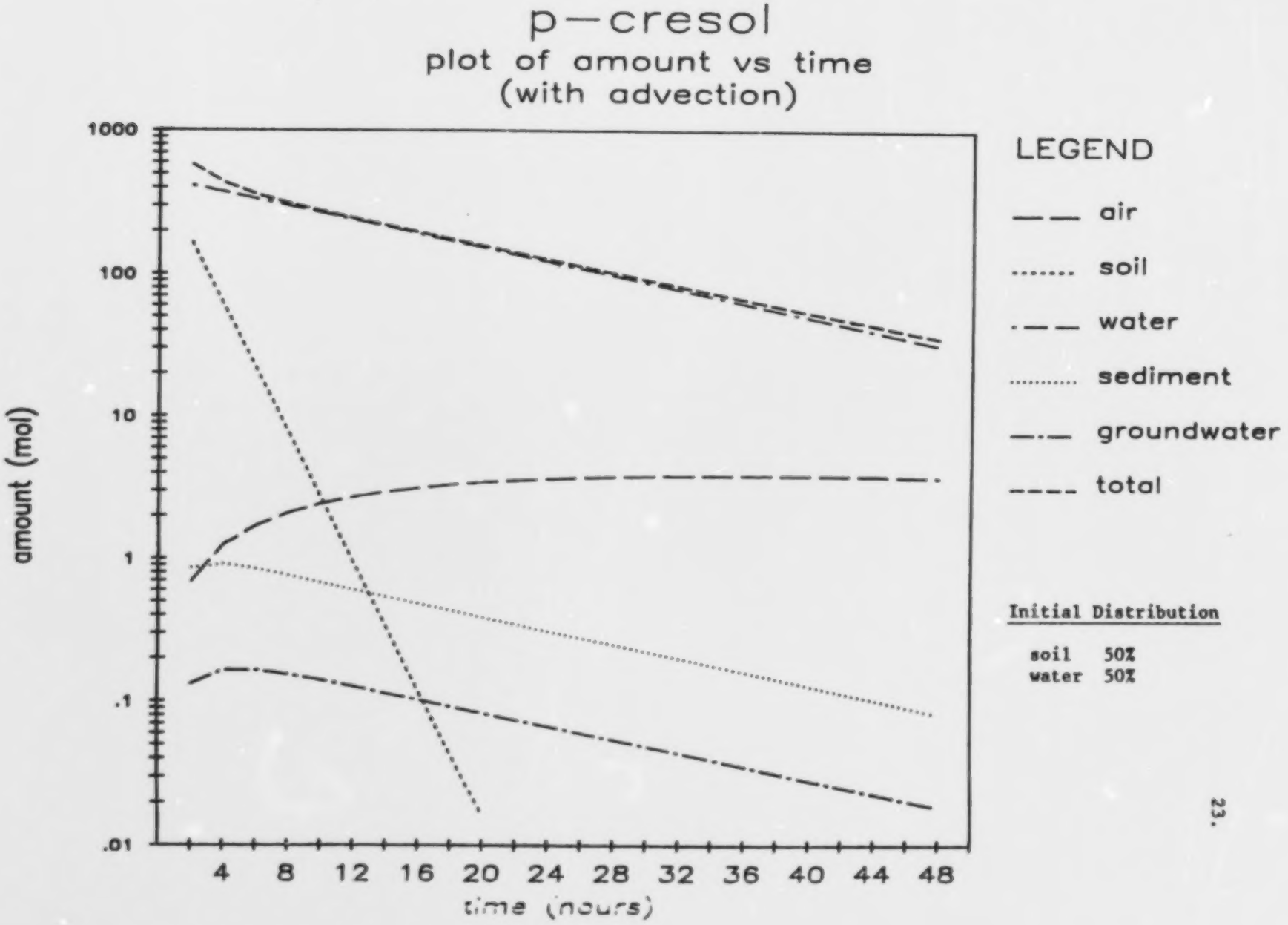

p-cresol
plot of amount vs time
(with advection)
amount (mol)
1000
100
10
1
.1
.01
4
8
12
16
20
24
28
32
36
40
44
48
time (hours)
LEGEND
air
soil
water
sediment
groundwater
total
Initial Distribution
soil 50%
water 50%

Figure 4.7

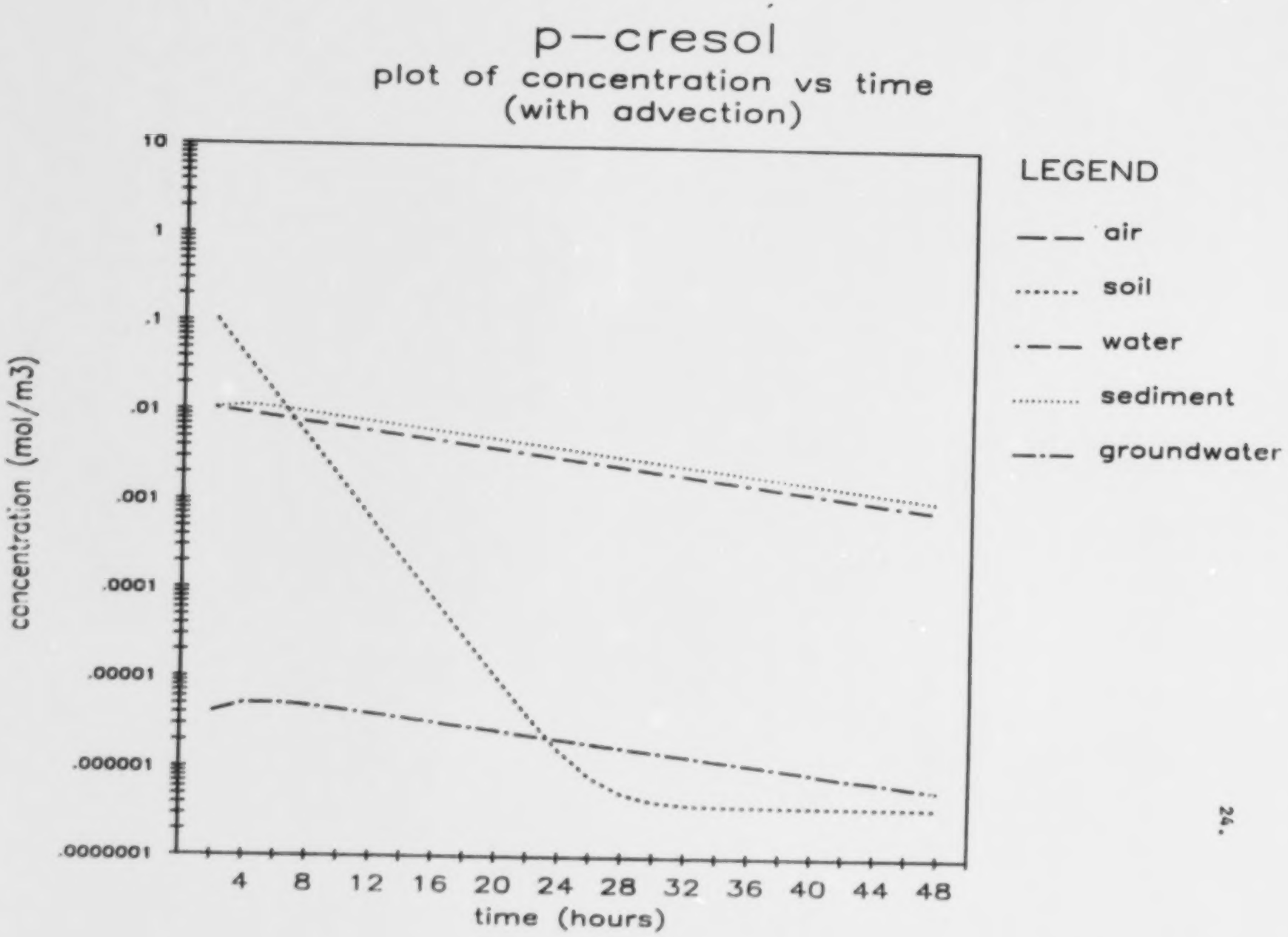

p-cresol
plot of concentration vs time
(with advection)
concentration (mol/m3)
10
1
.1
.01
.001
.0001
.00001
.000001
.0000001
4
8
12
16
20
24
28
32
36
40
44
48
time (hours)
LEGEND
air
soil
water
sediment
groundwater

Figure 4.8

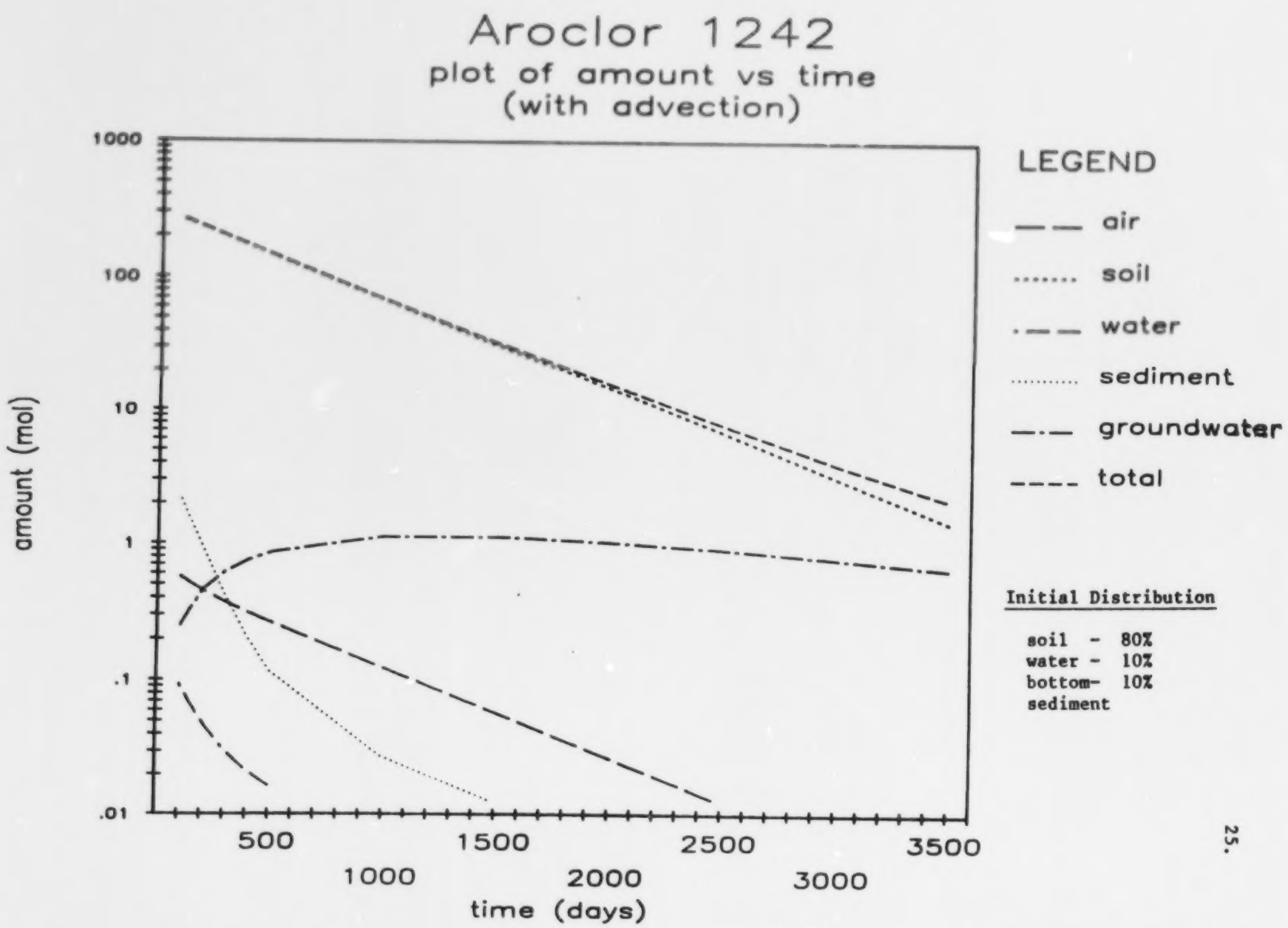

Aroclor 1242
plot of amount vs time
(with advection)
amount (mol)
1000
100
10
1
.1
.01
500
1000
1500
2000
2500
3000
3500
time (days)
LEGEND
air
soil
water
sediment
groundwater
total
Initial Distribution
soil - 80%
water - 10%
bottom- 10%
sediment

Figure 4.9

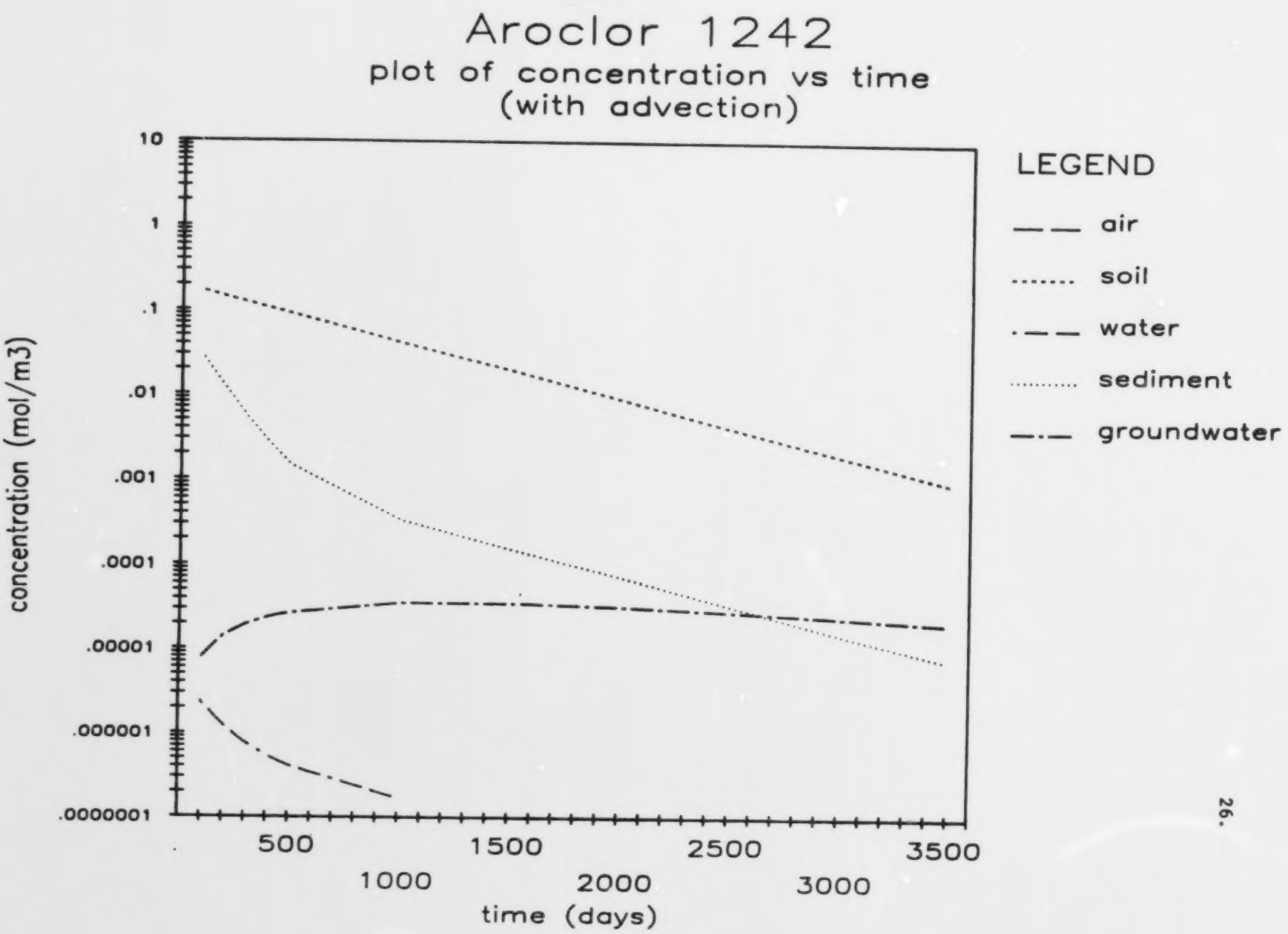

Aroclor 1242
plot of concentration vs time
(with advection)
concentration (mol/m3)
10
1
.1
.01
.001
.0001
.00001
.000001
.0000001
500
1000
1500
2000
2500
3000
3500
time (days)
LEGEND
air
soil
water
sediment
groundwater

Figure 4.10

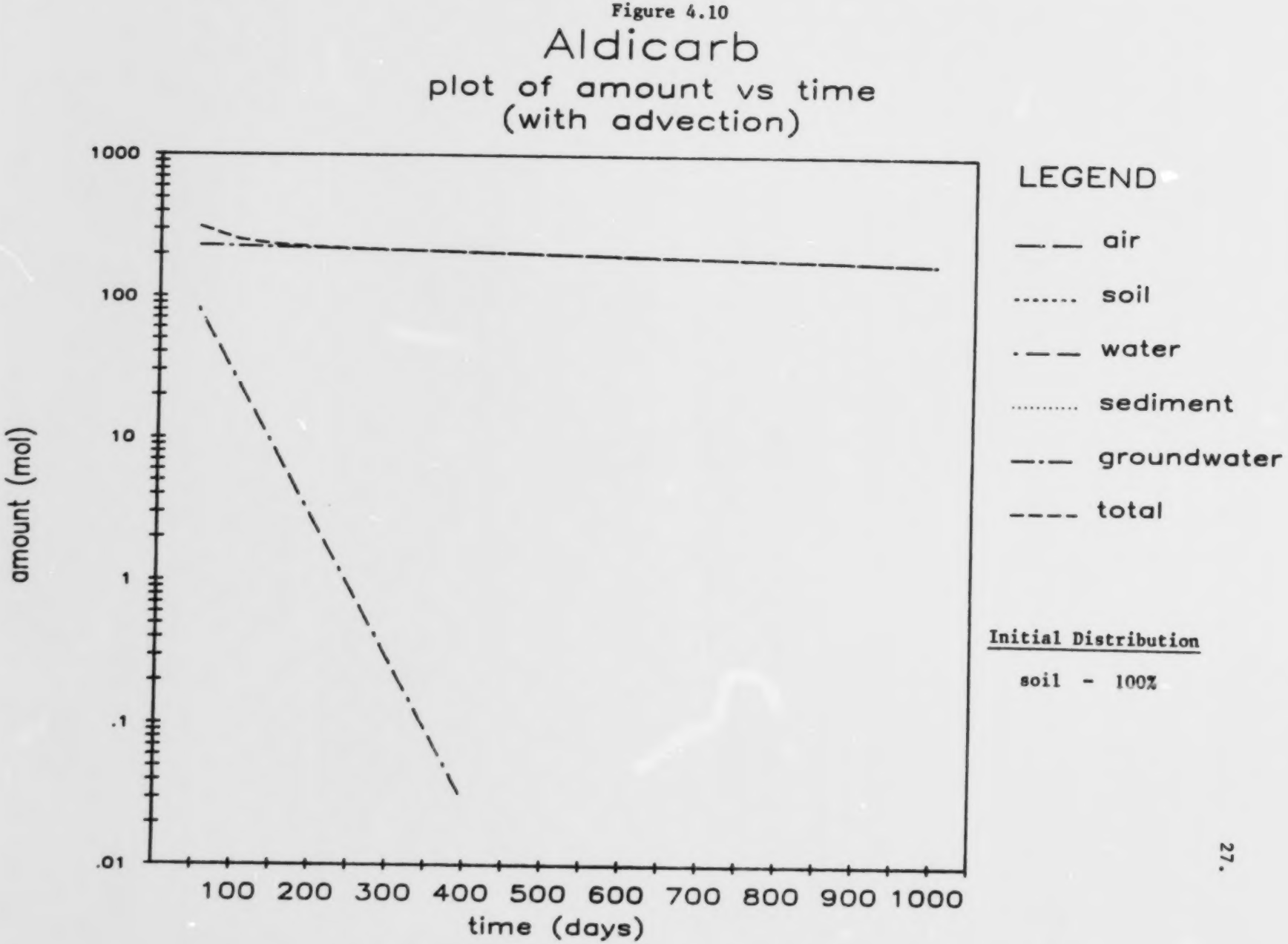

Aldicarb
plot of amount vs time
(with advection)
amount (mol)
1000
100
10
1
.1
.01
100 200 300 400 500 600 700 800 900 1000
time (days)
LEGEND
air
soil
water
sediment
groundwater
total
Initial Distribution
soil - 100%

Figure 4.11

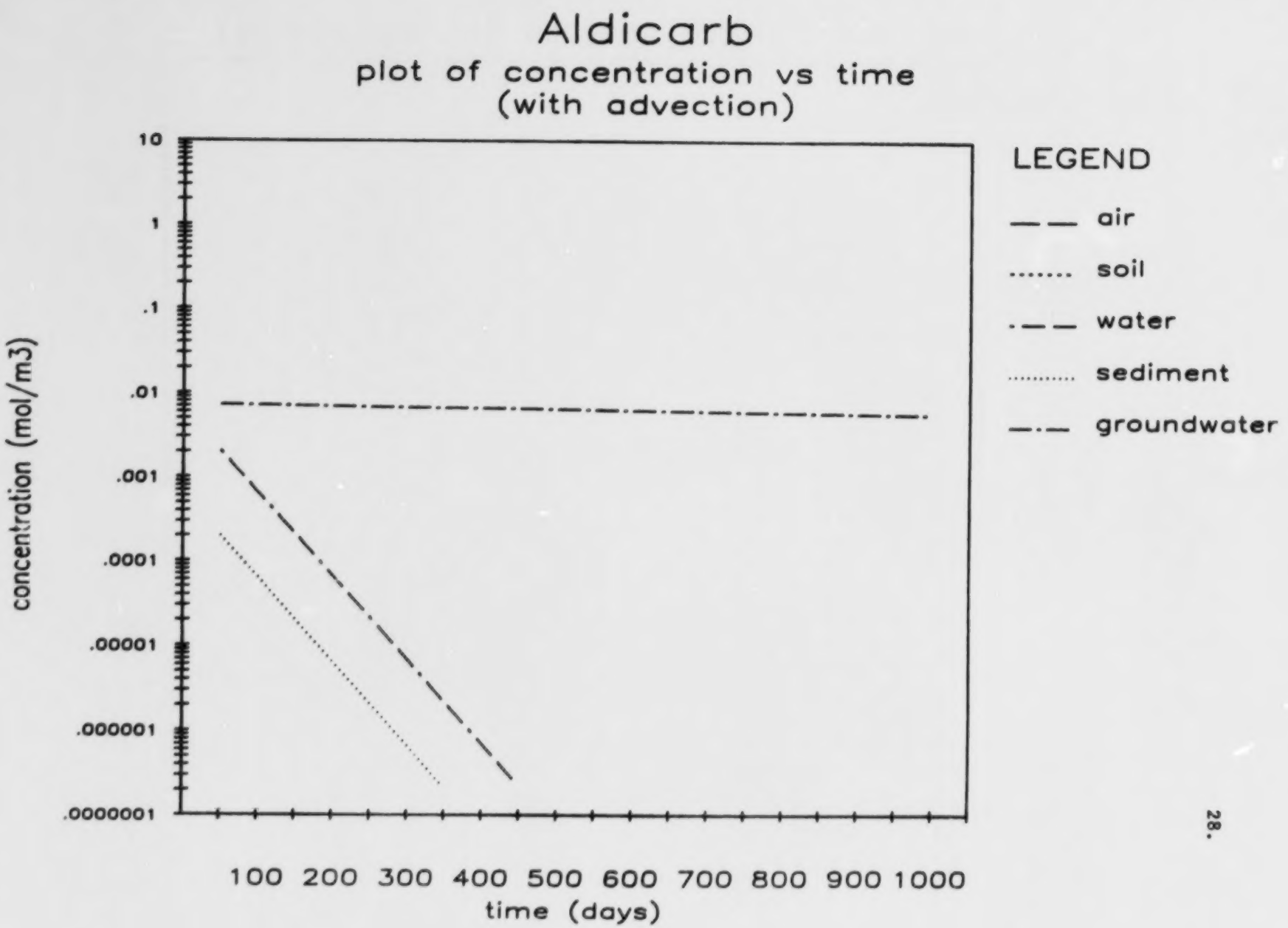

Aldicarb
plot of concentration vs time
(with advection)
concentration (mol/m3)
10
1
.1
.01
.001
.0001
.00001
.000001
.0000001
100 200 300 400 500 600 700 800 900 1000
time (days)
LEGEND
air
soil
water
sediment
groundwater

Figure 4.12

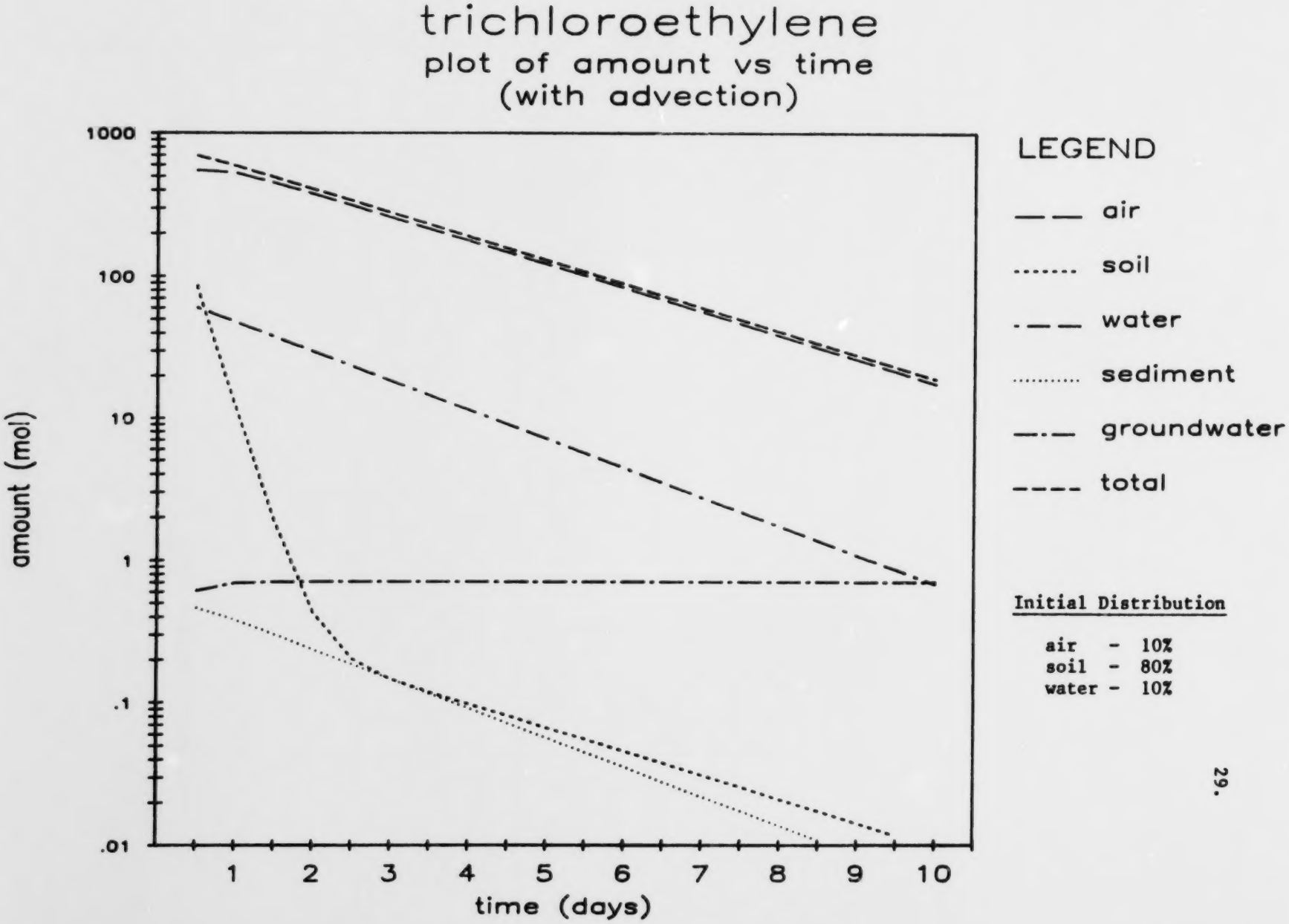

trichloroethylene
plot of amount vs time
(with advection)
amount (mol)
1000
100
10
1
.1
.01
1
2
3
4
5
6
7
8
9
10
time (days)
LEGEND
air
soil
water
sediment
groundwater
total
Initial Distribution
air - 10%
soil - 80%
water - 10%

Figure 4.13

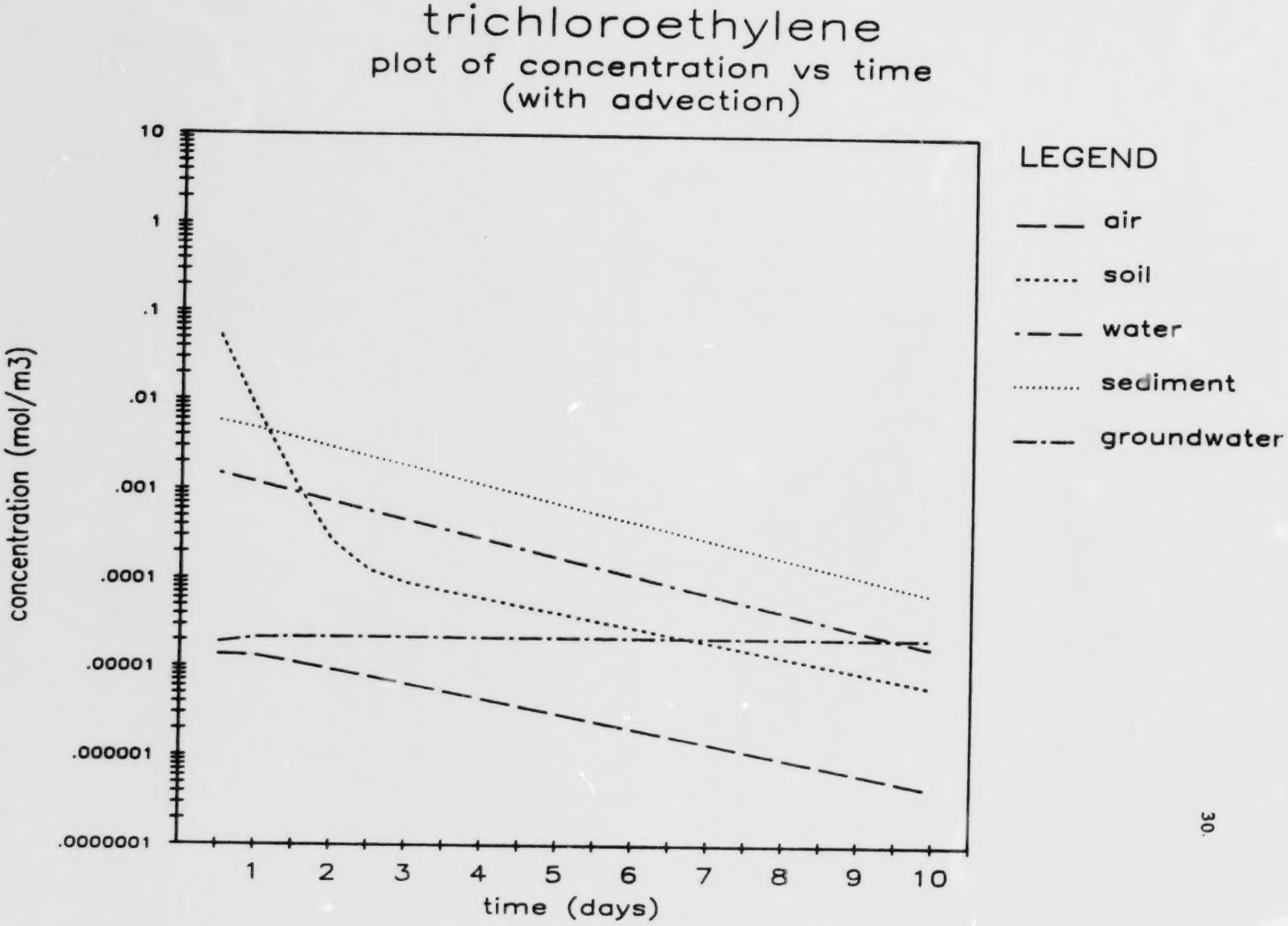

trichloroethylene
plot of concentration vs time
(with advection)
concentration (mol/m3)
10
1
.1
.01
.001
.0001
.00001
.000001
.0000001
1
2
3
4
5
6
7
8
9
10
time (days)
LEGEND
air
soil
water
sediment
groundwater

Figure 4.14

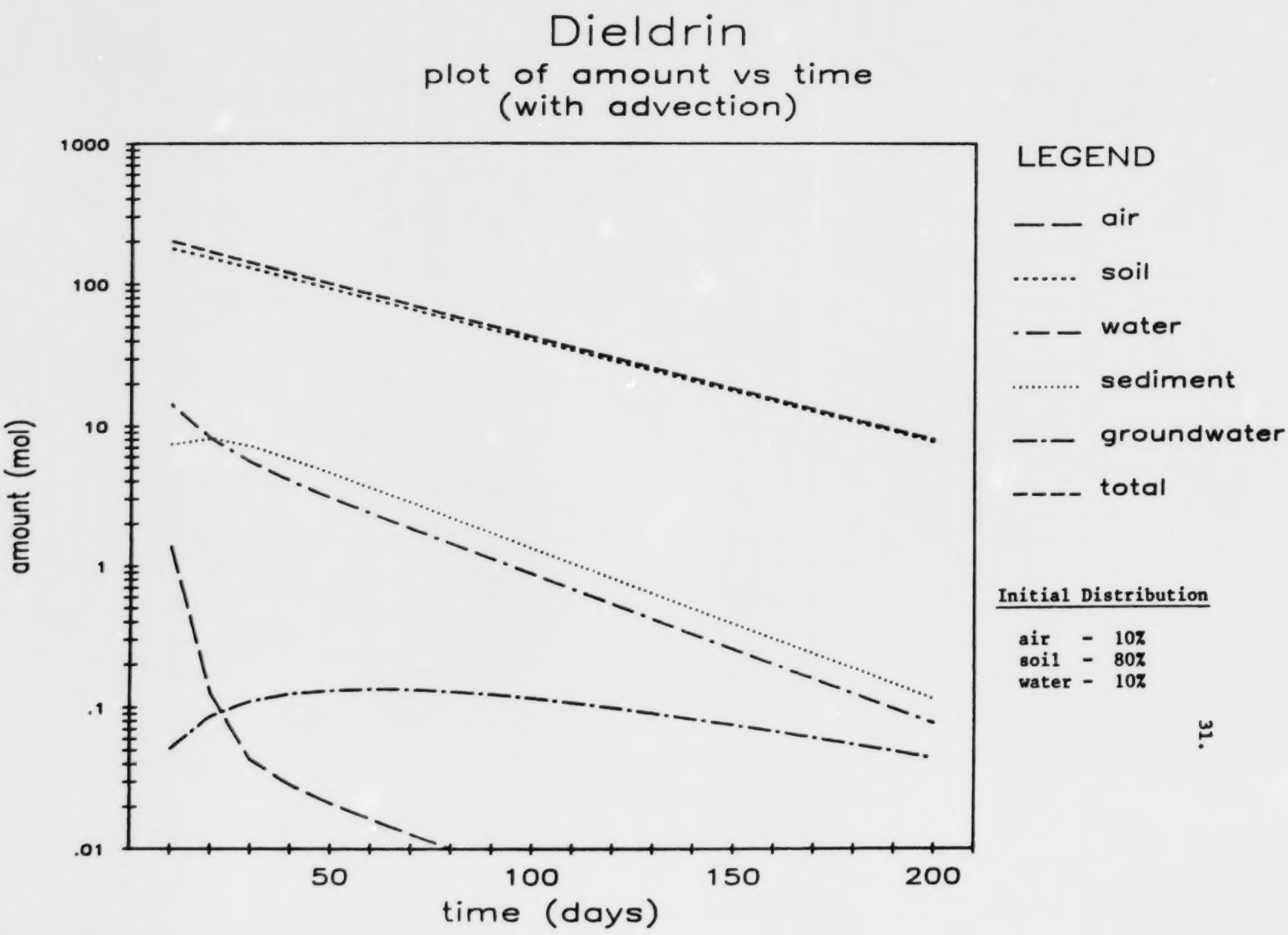

Dieldrin
plot of amount vs time
(with advection)
amount (mol)
1000
100
10
1
.1
.01
50
100
150
200
time (days)
LEGEND
air
soil
water
sediment
groundwater
total
Initial Distribution
air - 10%
soil - 80%
water - 10%

Figure 4.15

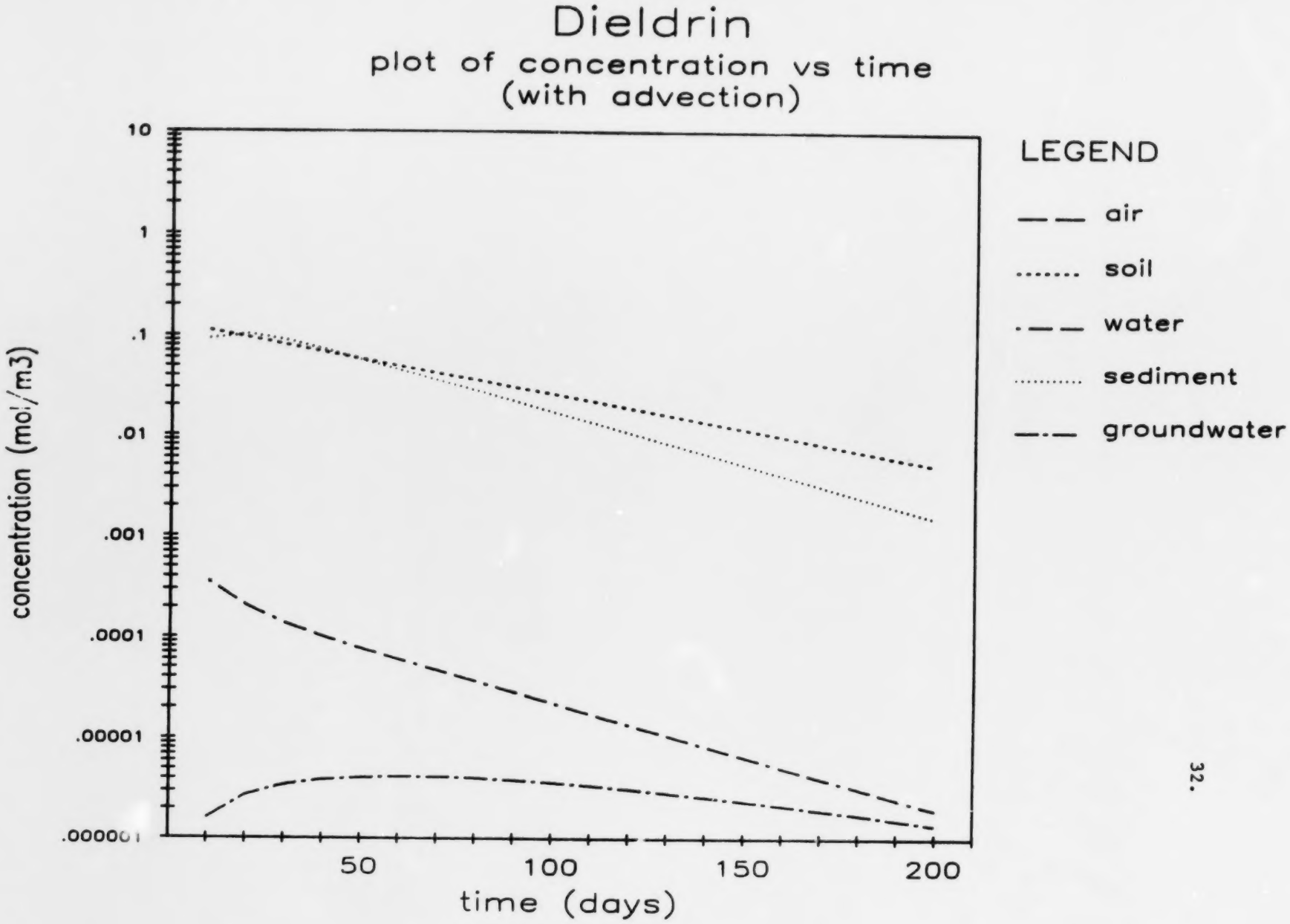

Dieldrin
plot of concentration vs time
(with advection)
concentration (mol/m3)
10
1
.1
.01
.001
.0001
.00001
.000001
50
100
150
200
time (days)
LEGEND
air
soil
water
sediment
groundwater

Figure 4.16

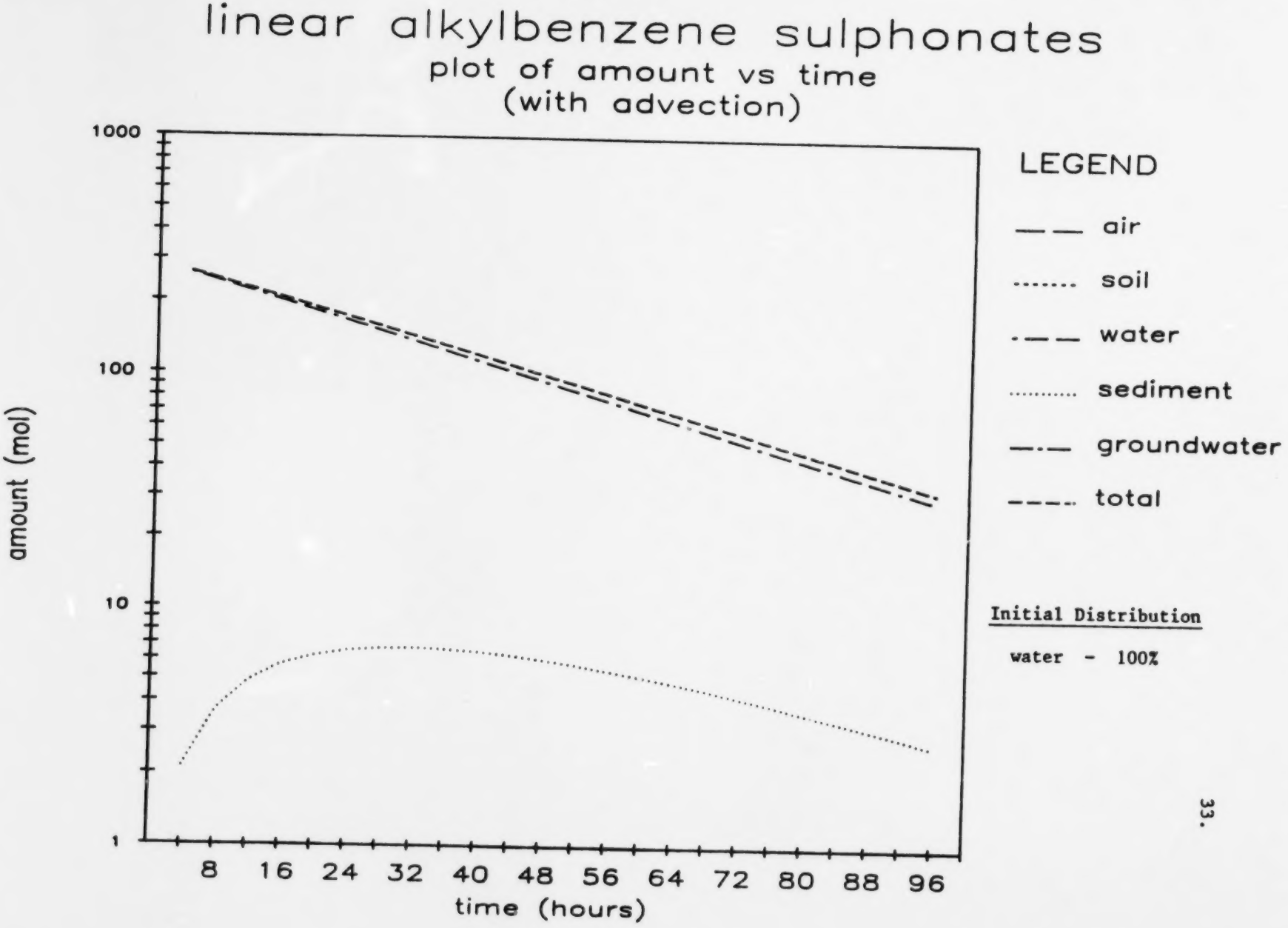

linear alkylbenzene sulphonates
plot of amount vs time
(with advection)
1000
100
10
1
amount (mol)
8
16
24
32
40
48
56
64
72
80
88
96
time (hours)
LEGEND
air
soil
water
sediment
groundwater
total
Initial Distribution
water - 100%

Figure 4.17

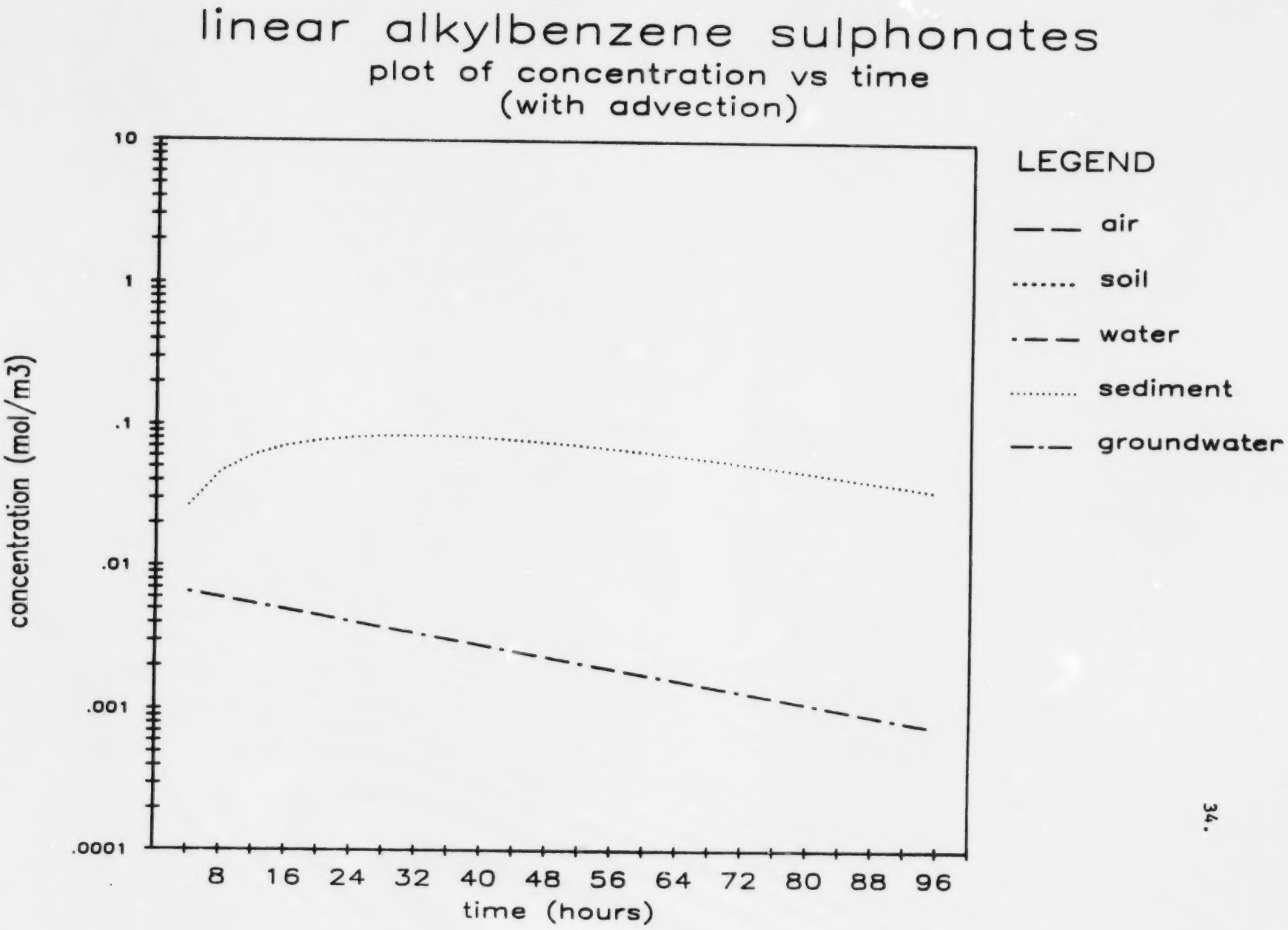

linear alkylbenzene sulphonates
plot of concentration vs time
(with advection)
concentration (mol/m3)
10
1
.1
.01
.001
.0001
8
16
24
32
40
48
56
64
72
80
88
96
time (hours)
LEGEND
air
soil
water
sediment
groundwater

Figure 4.18

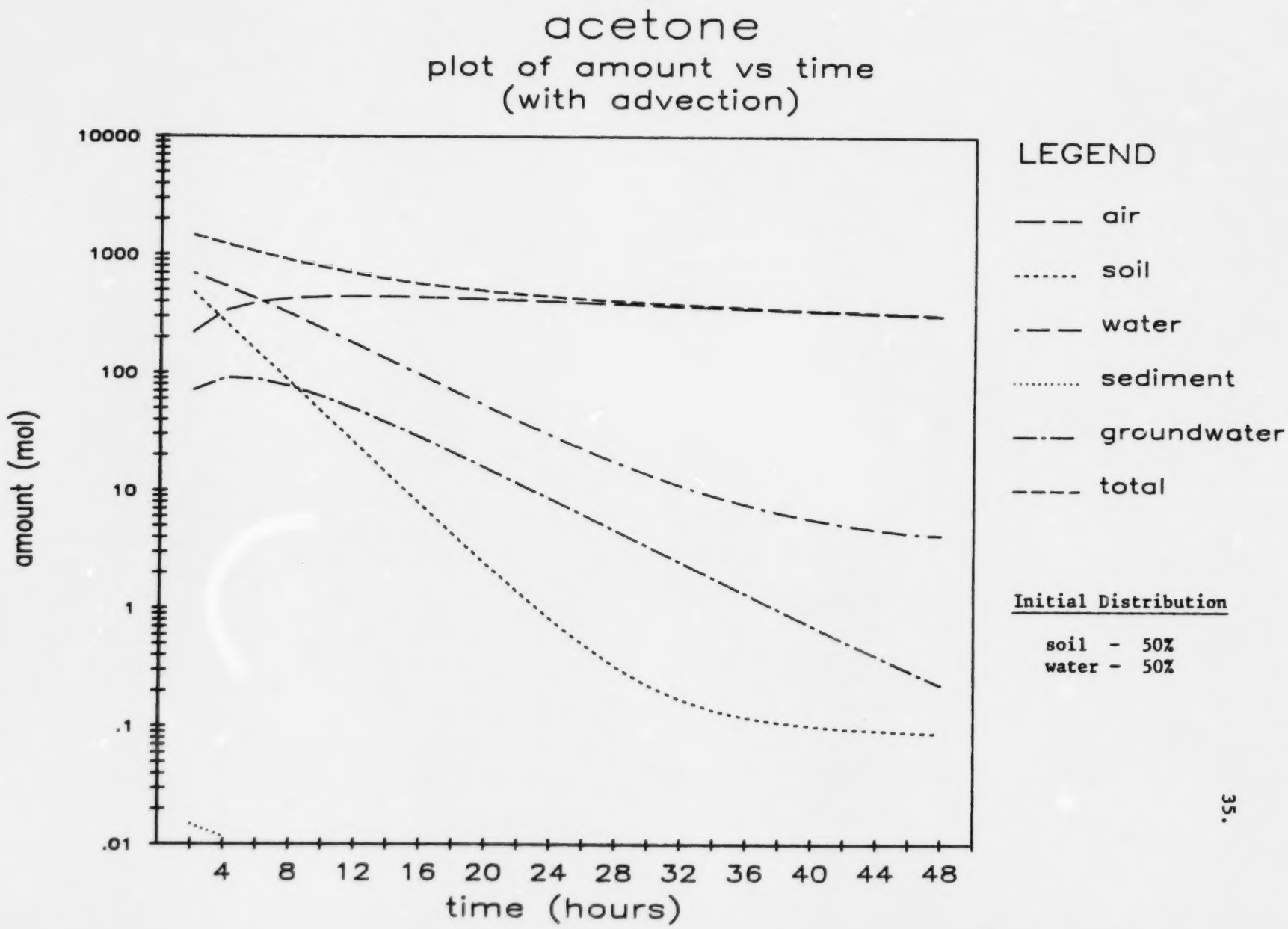

acetone
plot of amount vs time
(with advection)
10000
1000
100
10
1
.1
.01
amount (mol)
4
8
12
16
20
24
28
32
36
40
44
48
time (hours)
LEGEND
air
soil
water
sediment
groundwater
total
Initial Distribution
soil - 50%
water - 50%

Figure 4.19

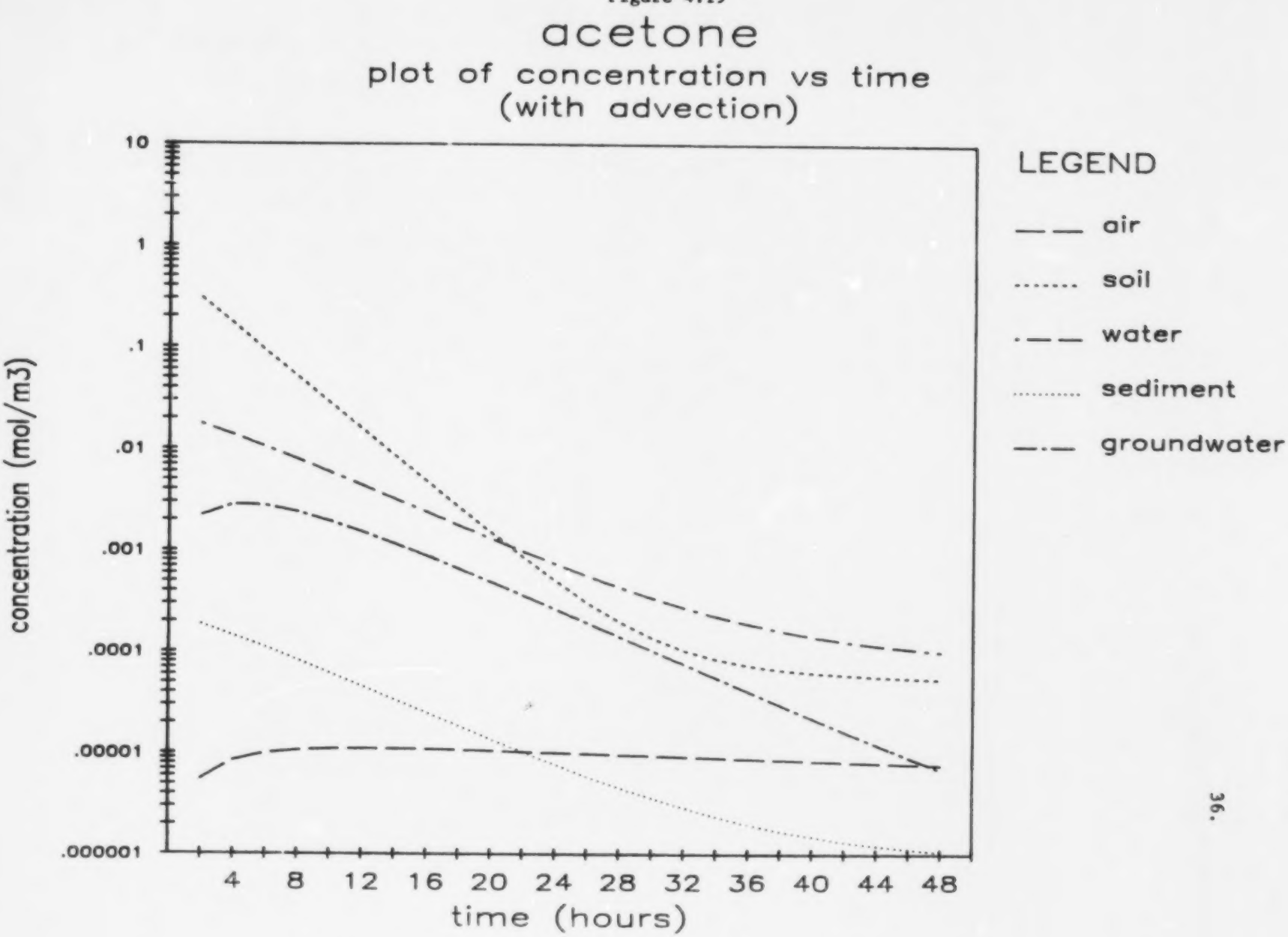

acetone
plot of concentration vs time
(with advection)
concentration (mol/m3)
10
1
.1
.01
.001
.0001
.00001
.000001
4
8
12
16
20
24
28
32
36
40
44
48
time (hours)
LEGEND
air
soil
water
sediment
groundwater

Figure 4.20. Specimen output for ethylene dichloride

```
COMPOUND PROPERTIES
CHEMICAL IS                                    ethylene dichloride
MOLECULAR WEIGHT (g/mol)                        98.96
AQUEOUS SOLUBILITY (g/m3)                       8500
VAPOUR PRESSURE (Pa)                            7000
LOG OCTANOL-WATER PARTITION COEFFICIENT         1.48
SOIL-WATER PARTITION COEFF. .9286349
BOTTOM SEDIMENT-WATER PARTITION COEFF. .557181
AIR-WATER PARTITION COEFF. 3.403583E-02

          REACTION HALF LIVES, TRANSFER TIMES, Z VALUES, EQUILIBRIUM PERCENT
AIR              2.400E+03    9.364E+01    4.176E-04    9.489E+01
SOIL             1.000E+06    1.320E+01    1.139E-02    1.035E-01
WATER            1.000E+06    5.422E+01    1.227E-02    2.788E+00
BOTTOM SEDIMENT  1.000E+06    5.572E-01    6.837E-03    3.106E-03
GROUNDWATER      1.000E+06    1.449E+06    1.227E-02    2.230E+00

FISH BCF AND Z VALUE            1.450E+00    1.779E-02
OVERALL APPROXIMATE HALF LIFE   7.149E+01

ADVECTIVE HALF LIVES (hours)
AIR                70
WATER              700

ENVIRONMENTAL PROPERTIES
TEMPERATURE (DEG C)                          15
LENGTH OF EVALUATIVE ENVIRONMENT (m)         200
WATER DEPTH (m) 5
FRACTION OF WATER                            .2

VOLUME OF AIR (CUBIC METRES)                 4E+07
VOLUME OF SOIL                               1600
VOLUME OF WATER                              40000
VOLUME OF BOTTOM SEDIMENT                    80
VOLUME OF GROUNDWATER                        32000

EMISSIONS (kg)  100 OR (mols) 1010.509
PERCENT IN SOIL          0
PERCENT IN WATER         100
PERCENT IN AIR           0
PERCENT IN SEDIMENT      0
PERCENT IN GROUNDWATER   0

time increment is  6   hours

TIME IS 48  HOURS OR  2  DAYS

COMPARTMENT     CONCENTRATION  FUGACITY      AMOUNT         PERCENT

AIR             1.012E-05      2.422E-02     4.046E+02      4.004E+01
SOIL            2.095E-04      1.839E-02     3.353E-01      3.318E-02
WATER           1.162E-02      9.470E-01     4.648E+02      4.600E+01
SEDIMENT        7.126E-03      1.042E+00     5.701E-01      5.641E-02
GROUNDWATER     1.858E-07      1.514E-05     5.945E-03      5.883E-04
REACTED                                      3.060E+00      3.028E-01
ADVECTED (AIR)                               1.041E+02      1.030E+01
ADVECTED (WATER)                             3.296E+01      3.261E+00
TOTAL                                        1.011E+03      1.000E+02
TOTAL IN SYSTEM                              8.704E+02

CONCENTRATION IN FISH                1.667E+00 ppm     1.684E-02 mol/m3
CONCENTRATION IN SUSPENDED SEDIMENT  9.611E-01 ppm     6.475E-03 mol/m3
```

5. DISCUSSION.

These illustrative results show convincingly that chemicals can range in persistence from a few hours to several years. This information is believed to be important in determining appropriate spill response actions since it may not be necessary to respond vigorously to a short lived chemical.

It is also clear that the chemicals show quite different partitioning tendencies. Particularly important is the tendency for evaporation.

The absolute concentration levels may be useful in certain cases, especially if other information is available on toxic levels or regulatory concentrations.

It appears that it is necessary to give information on both concentration and amount since each has important features. It would be useful to display transfer and reaction processes, possibly as graphs, bar charts or pie charts since this would give the on-scene personnel some insight into the chemical's migration tendencies following a spill. It may be possible to generate this output in narrative form, indeed a case can be made for generating the entire output in narrative form since it is easier to print text than graphs or diagrams.

Plots of fugacity are of interest to the modeller rather than to the on-scene personnel and are probably not necessary.

The transport parameter values and the compartment volumes appear to be reasonable, but some refinement may be needed. In some cases it is suspected that groundwater contamination is exaggerated and it may be desirable to slow the process of water flow from soil to groundwater. It is noteworthy that there is no provision for transport out of groundwater; thus it is a "dead end". If the chemical does not react in groundwater, there will be residues present in that compartment indefinitely. The inclusion of air and water advection is clearly desirable since it gives more realistic output. Its inclusion introduces possible confusion between loss due to reaction and due to advection. This information could perhaps be provided in narrative form.

In general, the model is regarded as being successful in that it is very robust, makes little memory or time demands and gives reasonable output. It is difficult for the authors to judge to what extent it is useful to

emergency personnel. Thus, it would be useful at this stage of development to obtain guidance or feedback from these personnel about the preferred format of the output and the information which would be most useful to them.

6. CONCLUSIONS.

A simple model has been devised which can be used on a portable microcomputer to predict the long-term behaviour of chemical spills.

It has been tested on 8 common chemicals and found to give a satisfactory output.

For implementation for emergency purposes it is desirable to obtain feedback from emergency personnel concerning the nature and format of the output which is of most value to them.

The most desirable single change in model structure would be to include a separate pure chemical phase associated with each compartment. This introduces a considerable mathematical complexity but it would give greater realism.

REFERENCES

Environment Canada (1984) EnviroTIPS, EPS, "Ethylene Dichloride".

Games, L.M. 1982 "Modeling the Fate of chemicals in the Aquatic Environment" p 325-346 Dickson, K.L., Maki, A.W. and Cairns, J. Jr. (Eds) Ann Arbor Science, Ann Arbor MI

Gutcho, S.J., (1977), "Surfactants and Sequestrants: Recent Advances", Noyes Data Corporation, Park Ridge, N.J.

Mackay, D., Paterson, S., Eisenreich, S.J., Simmons, M.S., (1983), "The Physical Behavior of PCBs in the Great Lakes", Ann Arbor Science, Ann Arbor, MI.

Mackay, D., Paterson, S. (1982) Environ. Sci. Technol. 16. 654A.

Mackay, D., Paterson, S., Cheung, B., Neely, W.B. (1985) "Evaluating the Environmental Behaviour of Chemicals with a Level III Fugacity Model". Chemosphere (in press).

Neely, W.B., Lutz, R.W. (1985), Proc. of Tech. Sem. on Chemical Spills, Environment Canada, Toronto, Canada.

Rao, P.S.C., Davidson, J.M. (1980), in "Environmental Impact of Nonpoint Source Pollution", Ann Arbor Science, Ann Arbor, MI.

Rathburn, R.E., Doyle, W.S., Shultz, D.J., Tai, D.Y. (1982). Chemosphere 11, 1097.

Schnoor, J.L., McAvoy, D.C. (1981), ASCE 107, EE6.

Smith, J.H., Mabey, W.R., Bohonos, N., Holt, B.R., Lee, S.S., Chou, T.-W., Bomberger, D.C., Mill, T., (1978). "Environmental Pathways of Selected Chemicals in Freshwater Systems", Vol. II, EPA-600/7-78-074.

Union Carbide, Material Data Sheet.

Verschueren, K. (1983), "Handbook of Environmental Data on Organic Chemicals", 2nd edition, Van Nostrand Reinhold Company, New York, N.Y.

APPENDIX

COMPOUND PROPERTIES

CHEMICAL IS	ethylene dichloride
MOLECULAR WEIGHT (g/mol)	98.96
AQUEOUS SOLUBILITY (g/m3)	8500
VAPOUR PRESSURE (Pa)	7000
LOG OCTANOL-WATER PARTITION COEFFICIENT	1.48
SOIL-WATER PARTITION COEFF. .9286349	
BOTTOM SEDIMENT-WATER PARTITION COEFF. .557181	
AIR-WATER PARTITION COEFF. 3.403583E-02	

	REACTION HALF LIVES,	TRANSFER TIMES,	Z VALUES,	EQUILIBRIUM PERCENT
AIR	2.400E+03	9.364E+01	4.176E-04	9.488E+01
SOIL	1.000E+06	1.320E+01	1.139E-02	1.035E-01
WATER	1.000E+06	5.422E+01	1.227E-02	2.788E+00
BOTTOM SEDIMENT	1.000E+06	5.572E-01	6.837E-03	3.106E-03
GROUNDWATER	1.000E+06	1.449E+06	1.227E-02	2.230E+00

FISH BCF AND Z VALUE	1.450E+00	1.779E-02
OVERALL APPROXIMATE HALF LIFE	7.149E+01	

ADVECTIVE HALF LIVES (hours)

AIR	70
WATER	700

ENVIRONMENTAL PROPERTIES

TEMPERATURE (DEG C)	15
LENGTH OF EVALUATIVE ENVIRONMENT (m)	200
WATER DEPTH (m)	5
FRACTION OF WATER	.2
VOLUME OF AIR (CUBIC METRES)	4E+07
VOLUME OF SOIL	1600
VOLUME OF WATER	40000
VOLUME OF BOTTOM SEDIMENT	80
VOLUME OF GROUNDWATER	32000

EMISSIONS (kg) 100 OR (mols) 1010.509

PERCENT IN SOIL	0
PERCENT IN WATER	100
PERCENT IN AIR	0
PERCENT IN SEDIMENT	0
PERCENT IN GROUNDWATER	0

time increment is 6 hours

TIME IS 48 HOURS OR 2 DAYS

COMPARTMENT	CONCENTRATION	FUGACITY	AMOUNT	PERCENT
AIR	1.012E-05	2.422E-02	4.046E+02	4.004E+01
SOIL	2.095E-04	1.839E-02	3.353E-01	3.318E-02
WATER	1.162E-02	9.470E-01	4.648E+02	4.600E+01
SEDIMENT	7.126E-03	1.042E+00	5.701E-01	5.641E-02
GROUNDWATER	1.858E-07	1.514E-05	5.945E-03	5.883E-04
REACTED			3.060E+00	3.028E-01
ADVECTED (AIR)			1.041E+02	1.030E+01
ADVECTED (WATER)			3.296E+01	3.261E+00
TOTAL			1.011E+03	1.000E+02
TOTAL IN SYSTEM			8.704E+02	

CONCENTRATION IN FISH	1.667E+00 ppm	1.684E-02 mol/m3
CONCENTRATION IN SUSPENDED SEDIMENT	9.611E-01 ppm	6.475E-03 mol/m3

```
 5 'A LONG TERM CHEMICAL SPILL MODEL
10 CLS
15 PRINT "WELCOME TO THE LONG TERM CHEMICAL SPILL FATE PROGRAM."
20 PRINT :PRINT "WE WILL FIRST INPUT THE CHEMICAL PROPERTIES"
25 INPUT "PLEASE INPUT THE CHEMICAL NAME";N$
30 INPUT "THE MOLECULAR WEIGHT IN g/mol, eg. 200";WM
35 INPUT "NOW THE AQUEOUS SOLUBILITY IN UNITS OF mg/L OR g/m3, eg 50";SG
40 INPUT "NOW THE VAPOUR PRESSURE IN PASCALS (NOTE THAT 1 ATM IS 101325 Pa AND 1
 mm Hg IS 133 Pa, eg 20";VP
45 INPUT "NOW THE LOG OCTANOL-WATER PARTITION COEFFICIENT, eg 3.5";LKOW
50 PRINT :PRINT "NOW THE CHEMICAL REACTION HALF LIVES IN HOURS IN EACH COMPARTME
NT, eg 100        DO NOT INPUT ZERO.  IF NO REACTION INSERT A LARGE NUMBER, EG 1E
06"
55 INPUT "IN AIR";HLA
60 INPUT "IN SOIL";HLS
65 INPUT "IN WATER";HLW
70 INPUT "IN BOTTOM SEDIMENT";HLB
75 INPUT "IN GROUNDWATER";HLG
80 PRINT :INPUT "PLEASE INPUT THE TOTAL CHEMICAL SPILL AMOUNT IN kg,eg 100";E
85 PRINT "NOW THE PERCENTS IN EACH COMPARTMENT eg 20"
90 INPUT "IN AIR";EA
95 INPUT "IN SOIL";ES
100 INPUT "IN WATER";EW
105 INPUT "IN BOTTOM SEDIMENT";EB
110 INPUT "IN GROUNDWATER";EG
115 PRINT :PRINT "NOW WE WILL INPUT THE ENVIRONMENTAL DIMENSIONS AND CONDITIONS"

120 INPUT "FIRST INPUT THE TEMPERATURE IN DEGREES C, eg 15";TC
125 INPUT "NOW THE DIMENSION OF THE SQUARE ENVIRONMENT IN METRES, eg 200";L
130 INPUT "NOW THE FRACTION OF THE AREA WHICH IS WATER, eg 0.2";WF
135 INPUT "NOW THE MEAN WATER DEPTH IN METRES eg 5";WD
140 'define advective half-lives in air and water
145 HLAA=70
150 HLWA=700
155 INPUT "THE PROGRAM INCORPORATES AN ADVECTIVE HALF-LIFE OF 70 HOURS IN AIR AN
D 700 HOURS IN WATER.  IF YOU WISH TO ELIMINATE THESE, ENTER 2";XX$
160 IF XX$="2" THEN GOTO 165 ELSE GOTO 170
165 HLAA=1000000!:HLWA=1000000!
170 KOW=10^LKOW
175 KOC=.41*KOW
180 WF=.2
185 VA=L*L*1000
190 VS=L*L*.05*(1-WF)
195 VW=L*L*WD*WF
200 VB=L*L*.01*WF
205 VG=L*L*1*(1-WF)
210 ZA=1/8.314/(TC+273)
215 ZW=SG/(VP*WM)
220 ZS=ZW*.05*KOC*1.5
225 ZB=ZW*.03*KOC*1.5
230 ZF=ZW*.048*KOW
235 BCF=ZF/ZW
240 KPS=ZS/ZW
245 KPB=ZB/ZW
250 KAW=ZA/ZW
255 ZG=ZW
260 DBA=L*L*(1-WF)*ZA*.1
```

```
265 DAS=DSA
270 DAW=L*L*WF/(1/ZA/10+1/ZW/.1)
275 DWA=DAW
280 DBW=L*L*WF*ZW*.01
285 DWB=DBW+ZB*.001*L*L*WF/(365*24)
290 DSW=ZW*.5*L*L*(1-WF)/(365*24)
295 DSG=ZW*.5*L*L*(1-WF)/(365*24)
300 DAR=VA*ZA*.69/HLA
305 DAV=VA*ZA*.69/HLAA
310 DSR=VS*ZS*.69/HLS
315 DWR=VW*ZW*.69/HLW
320 DWV=VW*ZW*.69/HLWA
325 DBR=VB*ZB*.69/HLB
330 DGR=VG*ZG*.69/HLG
335 TS=VS*ZS/(DSA+DSW+DSG+DSR)
340 TA=VA*ZA/(DAS+DAW+DAR+DAV)
345 TW=VW*ZW/(DWA+DWB+DWR+DWV)
350 TB=VB*ZB/(DBW+DBR)
355 TG=VG*ZG/(DGR)
360 PRINT :PRINT "WE NOW SELECT THE CALCULATION TIME INCREMENT IN HOURS.  IT SHO
ULD PREFERABLY BE SMALLER THAN ANY OF THE FOLLOWING TIME CONSTANTS:"
365 PRINT TA,TS,TW,TB,TG
370 WIDTH "lpt1:",80
375 INPUT DT
380 PRINT :INPUT "HOW FREQUENTLY DO YOU WISH A PRINT OUT, eg FOR EVERY 96 HOURS:
  PREFERABLY A MULTIPLE OF THE TIME INCREMENT.";LOOP
385 INPUT "AT WHAT TIME IN DAYS DO YOU WANT THE CALCULATION TO STOP, eg 365";STO

390 NL=INT(LOOP/DT)
395 NS=INT(STO*24/LOOP)
400 VZA=VA*ZA
405 VZS=VS*ZS
410 VZW=VW*ZW
415 VZG=VG*ZG
420 VZB=VB*ZB
425 VZT=VZA+VZS+VZW+VZB+VZG
430 QA=100*VZA/VZT
435 QS=100*VZS/VZT
440 QW=100*VZW/VZT
445 QG=100*VZG/VZT
450 QB=100*VZB/VZT
455 HLT=VZT/(VZA/HLA+VZS/HLS+VZW/HLW+VZB/HLB+VZG/HLB+VZA/HLAA+VZW/HLWA)
460 'PRINT OUT OF INPUT DATA
465 LPRINT "COMPOUND PROPERTIES                                    "
470 LPRINT "CHEMICAL IS ";TAB(45) N$
475 LPRINT "MOLECULAR WEIGHT (g/mol)                               ";WM
480 LPRINT "AQUEOUS SOLUBILITY (g/m3)                               ";SG
485 LPRINT "VAPOUR PRESSURE (Pa)                                   ";VP
490 LPRINT "LOG OCTANOL-WATER PARTITION COEFFICIENT                 ";LKOW
495 LPRINT "SOIL-WATER PARTITION COEFF.";KPS
500 LPRINT "BOTTOM SEDIMENT-WATER PARTITION COEFF.";KPB
505 LPRINT "AIR-WATER PARTITION COEFF.";KAW
510 LPRINT
515 LPRINT "        REACTION HALF LIVES, TRANSFER TIMES, Z VALUES, EQUILIBRIUM P
ERCENT"
520 LPRINT "AIR";TAB(18);
```

```
525 LPRINT USING "##.###^^^^    ";HLA,TA,ZA,QA
530 LPRINT "SOIL";TAB(18);
535 LPRINT USING "##.###^^^^    ";HLS,TS,ZS,QS
540 LPRINT "WATER";TAB(18);
545 LPRINT USING "##.###^^^^    ";HLW,TW,ZW,QW
550 LPRINT "BOTTOM SEDIMENT";TAB(18);
555 LPRINT USING "##.###^^^^    ";HLB,TB,ZB,QB
560 LPRINT "GROUNDWATER";TAB(18);
565 LPRINT USING "##.###^^^^    ";HLG,TG,ZG,QG
570 LPRINT " "
575 LPRINT "FISH BCF AND Z VALUE";TAB(32);
580 LPRINT USING "##.###^^^^    ";BCF,ZF
585 LPRINT "OVERALL APPROXIMATE HALF LIFE";TAB(32);
590 LPRINT USING "##.###^^^^    ";HLT
595 LPRINT " "
600 LPRINT "ADVECTIVE HALF LIVES (hours)"
605 LPRINT "AIR";TAB(19) HLAA
610 LPRINT "WATER";TAB(19) HLWA:LPRINT " "
615 LPRINT "ENVIRONMENTAL PROPERTIES"
620 LPRINT "TEMPERATURE (DEG C)                          ";TC
625 LPRINT "LENGTH OF EVALUATIVE ENVIRONMENT (m)";L
630 LPRINT "WATER DEPTH (m)";WD
635 LPRINT "FRACTION OF WATER                            ";WF
640 LPRINT " "
645 LPRINT "VOLUME OF AIR (CUBIC METRES)                 ";VA
650 LPRINT "VOLUME OF SOIL                               ";VS
655 LPRINT "VOLUME OF WATER                              ";VW
660 LPRINT "VOLUME OF BOTTOM SEDIMENT                    ";VB
665 LPRINT "VOLUME OF GROUNDWATER                        ";VG
670 LPRINT
675 E=EK*1000/WM
680 MS=E*(ES+.000001)/100:FS=MS/(VS*ZS)
685 MA=E*(EA+.000001)/100:FA=MA/(VA*ZA)
690 MW=E*(EW+.000001)/100:FW=MW/(VW*ZW)
695 MB=E*(EB+.000001)/100:FB=MB/(VB*ZB)
700 MG=E*(EG+.000001)/100:FG=MG/(VG*ZG)
705 LPRINT "EMISSIONS (kg) ";EK "OR (mols)";E
710 LPRINT "PERCENT IN SOIL         ";ES
715 LPRINT "PERCENT IN WATER        ";EW
720 LPRINT "PERCENT IN AIR          ";EA
725 LPRINT "PERCENT IN SEDIMENT     ";EB
730 LPRINT "PERCENT IN GROUNDWATER ";EG
735 LPRINT
740 MR=0
745 TH=0
750 FDS=(FA*DAS-FS*(DSA+DSW+DSG+DSR))
755 FDA=(FS*DSA+FW*DWA-FA*(DAS+DAW+DAR+DAV))
760 FDW=(FA*DAW+FS*DSW+FB*DBW-FW*(DWA+DWS+DWB+DWR+DWV))
765 FDB=(FW*DWB-FB*(DBW+DBR))
770 FDG=(FS*DSG-FG*(DGR))
775 FOR J=1 TO NS
780 FOR I=1 TO NL
785 DMS=TS*FDS*(1-EXP(-DT/TS))
790 DMA=TA*FDA*(1-EXP(-DT/TA))
795 DMW=TW*FDW*(1-EXP(-DT/TW))
800 DMB=TB*FDB*(1-EXP(-DT/TB))
```

```
805 DMG=TG*FDG*(1-EXP(-DT/TG))
810 'CALCULATE TRANSFERS & TRANSFORMATION
815 DMSW=DMS*FS*DSW/FDS
820 DMSG=DMS*FS*DSG/FDS
825 DMSR=DMS*FS*DSR/FDS
830 DMWR=DMW*FW*DWR/FDW
835 DMWV=DMW*FW*DWV/FDW
840 DMBR=DMB*FB*DBR/FDB
845 DMAR=DMA*FA*DAR/FDA
850 DMAV=DMA*FA*DAV/FDA
855 DMGR=DMG*FG*DGR/FDG
860 IF (DMS/FDS)<(DMA/FDA) THEN Q=(DMS/FDS) ELSE Q=(DMA/FDA)
865 DMSA=(FS*DSA-FA*DAS)*Q:DMAS=-DMSA
870 IF (DMW/FDW)<(DMA/FDA) THEN Q=(DMW/FDW) ELSE Q=(DMA/FDA)
875 DMWA=(FW*DWA-FA*DAW)*Q:DMAW=-DMWA
880 IF (DMW/FDW)<(DMB/FDB) THEN Q=(DMW/FDW) ELSE Q=(DMB/FDB)
885 DMWB=(FW*DWB-FB*DBW)*Q:DMBW=-DMWB
890  CALCULATE NEW AMOUNTS
895 MS=MS-DMSG-DMSA-DMSW-DMSR
900 MA=MA-DMAS-DMAW-DMAR-DMAV
905 MW=MW-DMWA-DMWB+DMSW-DMWR-DMWV
910 MB=MB-DMBW-DMBR
915 MG=MG+DMSG-DMGR
920 MR=MR+DMSR+DMAR+DMWR+DMBR+DMGR
925 MAVT=MAVT+DMAV
930 MAWT=MAWT+DMWV
935 'CALCULATE FUGACITY &CONCENTRATION
940 CS=MS/VS:FS=CS/ZS:PS=100*MS/E
945 CA=MA/VA:FA=CA/ZA:PA=100*MA/E
950 CW=MW/VW:FW=CW/ZW:PW=100*MW/E
955 CG=MG/VG:FG=CG/ZG:PG=100*MG/E
960 CB=MB/VB:FB=CB/ZB:PB=100*MB/E
965 PR=100*MR/E
970 PVA=100*MAVT/E
975 PVW=100*MAWT/E
980 CFM=FW*ZF:CFP=CFM*WM
985 CSSM=FW*ZB:CSSF=CSSM*WM*1.5
990 TH=TH+DT:TD=TH/24
995 MT=MA+MS+MW+MB+MG+MR+MAVT+MAWT:MTS=MT-MR-MAVT-MAWT
1000 PT=100*MT/E
1005 NEXT I
1010 'PRINT OUT CONDITION
1015 LPRINT "time increment is ";DT;"  hours":LPRINT " "
1020 LPRINT "TIME IS";TH;" HOURS OR ";TD" DAYS":LPRINT " "
1025 LPRINT "COMPARTMENT    CONCENTRATION  FUGACITY        AMOUNT          PERCENT
"
1030 LPRINT
1035 LPRINT "AIR";TAB(15);
1040 LPRINT USING "##.###^^^^      ";CA;FA;MA;PA
1045 LPRINT "SOIL";TAB(15);
1050 LPRINT USING "##.###^^^^      ";CS;FS;MS;PS
1055 LPRINT "WATER";TAB(15);
1060 LPRINT USING "##.###^^^^      ";CW;FW;MW;PW
1065 LPRINT "SEDIMENT";TAB(15);
```

```
1070 LPRINT USING "##.###^^^^      ";CB;FB;MB;PB
1075 LPRINT "GROUNDWATER";TAB(15);
1080 LPRINT USING "##.###^^^^      ";CG;FG;MG;PG
1085 LPRINT "REACTED";TAB(45);
1090 LPRINT USING "##.###^^^^      ";MR;PR
1095 LPRINT "ADVECTED (AIR)";TAB(45);
1100 LPRINT USING "##.###^^^^      ";MAVT;PVA
1105 LPRINT  "ADVECTED (WATER)";TAB(45);
1110 LPRINT USING "##.###^^^^      ";MAWT;PVW
1115 LPRINT "TOTAL";TAB(45);
1120 LPRINT USING "##.###^^^^      ";MT;PT
1125 LPRINT "TOTAL IN SYSTEM";TAB(45);
1130 LPRINT USING "##.###^^^^                              ";MTS
1135 LPRINT " ":LPRINT " "
1140 LPRINT "CONCENTRATION IN FISH";TAB(37);
1145 LPRINT USING "##.###^^^^ ppm     ";CFP;
1150 LPRINT USING "##.###^^^^ mol/m3";CFM
1155 LPRINT "CONCENTRATION IN SUSPENDED SEDIMENT";TAB(37);
1160 LPRINT USING "##.###^^^^ ppm     ";CSSP;
1165 LPRINT USING "##.###^^^^ mol/m3";CSSM
1170 LPRINT " ":LPRINT " "
1175 NEXT J
```